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THE MANUFACTURE OF ACIDS AND ALKALIS

By George Lunge, Ph.D., Dr.Ing.
Emeritus Professor of Technical Chemistry, Zurich.

Completely Revised and Rewritten under the Editorship of
ALEXANDER CHARLES CUMMING
O.B.E., D.Sc, F.I.C.

VOLUME II

The Manufacture of Sulphuric Acid

(Chamber-Process)

THE MANUFACTURE OF SULPHURIC ACID (CHAMBER-PROCESS)

BY

WILFRID WYLD

CONSULTING CHEMIST

FORMERLY GENERAL TECHNICAL MANAGER OF MESSRS NICHOLSON AND SONS, LTD.
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FORMERLY MANAGER THE DHARAMSI MORARJI CHEMICAL CO., LTD., BOMBAY

GURNEY AND JACKSON
LONDON: 33 PATERNOSTER ROW
EDINBURGH: TWEEDDALE COURT
1924

PRINTED IN GREAT BRITAIN BY
OLIVER AND BOYD, EDINBURGH

EDITOR'S PREFACE

THE first English edition of Lunge's *Sulphuric Acid and Alkali* appeared in 1879. Since that date the book has been revised and extended in subsequent editions until, with the companion volumes on *Coal Tar and Ammonia*, it extended to nine volumes, covering most of the heavy chemical industries of Britain. A supplementary volume on Sulphuric and Nitric Acids by Dr Lunge in 1917 marked the end of his long labours in this field, and he informed the publishers that he could no longer undertake the preparation of new editions. The mere compilation of the volumes which he wrote would be in itself a wonderful achievement, but Dr Lunge's place in the history of chemical industry is due still more to the fact that he played a leading part in the discoveries and improvements which built up the industries of which he wrote.

By a curious coincidence, the end of Dr Lunge's long literary labours came just as the processes which he originally described died out. The Hargreaves process has gone, in this country at least; the Leblanc process is dying, if not actually dead already; even the chamber-process for sulphuric acid has now a competitor that threatens to become a rival.

The volumes written by Dr Lunge have escaped a common criticism of factory managers that books give only an outline of a manufacturing process; indeed, the only criticism has been that Dr Lunge's books gave almost too much detail. It may, however, be realised how important is a detail relating to a matter involving a possible saving of only one-tenth of one per cent., when it is pointed out that this small economy in the

manufacture of sulphuric acid would mean a saving of thousands of pounds, since the value of the sulphuric acid manufactured annually in Great Britain alone amounts to several million pounds.

Each new edition of this series has been an expansion and extension of that which preceded it, fuller treatment being accorded to subsidiary manufactures as they increased in commercial importance, until the name *Sulphuric Acid and Alkali* became a cover for what was practically an encyclopedia of the heavy chemical industries.

The last arrangement into volumes and parts was largely fortuitous, having arisen from uneven growth of knowledge and commercial development in different branches; and as this appeared to be a favourable opportunity for instituting a new arrangement, it was decided to subdivide the work into sections more in accord with modern developments. The last few years have brought with them many changes in the chemical industries, and the revision required in most of the volumes has involved such drastic recasting that the new edition will be more a new book than a revised edition.

It is doubtful if any one man could take up Dr Lunge's task of describing adequately all the industries now dealt with in these volumes, and it is certain that few would care to attempt it. Each volume will therefore be on a special subject and dealt with by a separate author, who is responsible for that volume, and is given a wide discretion in his treatment of the subject.

It is hoped that these united efforts will produce a new edition worthy of the great tradition which Dr Lunge has established.

The editor will be pleased to consider for publication in this series any manuscripts or original work on this, or allied subjects.

A. C. C.

AUTHOR'S PREFACE

THE previous edition of this work, which appeared in 1913, dealt not only with the chamber-process for the manufacture of sulphuric acid but also with the concentration of the acid and with the contact-process of manufacture. In order to permit of fuller treatment, the description of the concentration (other than the work done in the Glover tower) and the manufacture of sulphuric acid by the contact-process have been made the subject of separate volumes in this series. On account of this rearrangement, it has been possible to include in this volume much new matter and to discuss more adequately modern developments in chamber-practice.

Since the last edition, many inventors have taken out patents for apparatus designed to replace the large and costly chambers, but up to the time of writing (1924) very little reliable data on the newer systems of acid production is obtainable. I am carrying out a very extensive series of investigations with a "tower" plant working on a commercial scale, and hope to publish my findings at an early date.

Although the text of this volume deals principally with the working of the chamber-system, the instructions or suggestions regarding the control of the process apply equally well when the newer plant is used.

As mentioned in my preface to Vol. I, I have thought it inadvisable to give many costs of plant and production of acid, owing to the high prices of materials and labour, which continue to fluctuate.

W. W.

MANCHESTER, *March* 1924.

CONTENTS

CHAPTER I

CONSTRUCTION OF THE LEAD CHAMBERS

PAGE

General Notes on the Erection of Lead-chambers . . . 2
Lead for Chambers 9
Special Ways of building Chambers 22
Buildings for containing Acid-chambers 32
Renewal of Chambers 35
Combination of Chambers to form Sets 38
Cubical Contents of Chambers 44
Intensive or High-pressure Style of Working . . 45
Cost of Repairs 49
Other Proposals for diminishing the Chamber space . . 52
Mechanical Gas-mixers 54
Special Types of Chambers 58
Intermediate ("Reaction") Towers 66
Other Apparatus on the Principle of Plate-towers . . . 74
Replacing the Lead-chambers entirely by other Apparatus, Towers, etc. 79
Chamber and Tower Fittings 97
Supply of Water to the Chambers 104
The Steam 104
Introduction of Water in the form of Spray . . 109
Production of the Draught in Acid-chambers 120
By Fans 127
Anemometers 136
General Remarks on the Measurement of the Draught . . 141
Calculation of the Volume of Chamber-gases according to Temperature and Moisture 142

CHAPTER II

THE RECOVERY OF THE NITROGEN COMPOUNDS

The Gay-Lussac Tower 146
The Coke Packing 151

PAGE

The Gay-Lussac Tower (contd.)
Distribution of the Acid Feed 159
Centralised Working of the Gay-Lussac Towers . . . 169

Pumping Apparatus for Acid 171
Acid-eggs 171
Pulsometers 174
Pumps 185
Air-lifts 191

Working the Gay-Lussac Tower 193

Various Plans for recovering the Nitre 205

Denitration of Nitrous Vitriol 206
By Steam or Hot Water 207

The Glover Tower 209
Construction of a Glover Tower 211
The Height of the Glover Tower 217
The Cubical Contents of the Glover Tower . . . 219
The Position of the Glover Tower 221
Working the Glover Tower 222

Denitration by other Means 233
Packings for Gay-Lussac and other Towers 234

CHAPTER III

THE CHAMBER-PROCESS

Starting the Chambers 252
Supply of Air 254
Supply of Water (Steam) 259
Supply of Nitre 266
Proposals for modifying the Ordinary Way of supplying the Chambers with Nitre 277
Temperature of the Chambers 278
Depth of Acid 283
General Remarks 284
Irregular Working. Loss of Nitre 284
Distribution of Gases and Rate of Formation in the various parts of the Chambers 290
Improvements proposed for Acid-chambers in accordance with the Investigations described above 295
Carbon Dioxide in Chamber-gases 295
Testing the Chamber Exits 296

Theory of the Formation of Sulphuric Acid by the Chamber-process . 308

CHAPTER IV

THE PURIFICATION OF SULPHURIC ACID

PAGE

The Impurities of Chamber-acid 335
Injurious Action of the Arsenic contained in Sulphuric Acid . . 338
Removal of Arsenic from the Acid 340
De-arsenication of Strong Sulphuric Acid 356
Purification from Nitrogen Oxides 361
from Selenium 363
Coloured Acid 367
Preparation of Chemically Pure Acid 368

CHAPTER V

ARRANGEMENT OF A SULPHURIC ACID WORKS ON THE CHAMBER PLAN; YIELDS AND COSTS

Yields and Costs of Sulphuric Acid Manufacture . . . 379
I. Consumption of Nitre 381
II. Yield of Acid, calculated as H_2SO_4 381
Cause of the Losses in Manufacturing 383
III. Costs 384
From Pyrites 386

CHAPTER VI

OTHER PROCESSES FOR MANUFACTURING SULPHURIC ACID

I. Processes dispensing with Nitre 388
By Electricity 389
II. From Sulphates 393
Employment of Bisulphates 397
III. Calcining Pyrites with Salt 400
IV. By producing Hydrochloric and Sulphuric Acids simultaneously . 401
V. From Sulphur Dioxide and Selenium Dioxide . . . 402
VI. Combination of the Contact-process and the Chamber-process . 402

CHAPTER VII

APPLICATIONS OF SULPHURIC ACID

Production in United States 404
World's Production of Sulphuric Acid 406

APPENDIX

PAGE

First Aid in Acid Burns 408
Sulphuric Acid Gravities at Various Temperatures . . . 410
Cements and Packings 412
Weight per yard of Lead Piping for Chemical Purposes . . 413
Weight of Sheet Lead 413

INDEX OF NAMES 415

INDEX OF SUBJECTS 421

THE MANUFACTURE OF
SULPHURIC ACID
BY THE
CHAMBER PROCESS

CHAPTER I

CONSTRUCTION OF THE LEAD-CHAMBERS

IN the lead-chamber sulphuric acid is formed by the interaction of atmospheric oxygen, sulphur dioxide, water, and oxides of nitrogen. The sulphur dioxide is oxidised by the oxygen of the air, oxides of nitrogen acting as catalysts, and the sulphur trioxide produced combines with water to give sulphuric acid.

(All the substances entering into the process are in the state of gas or vapour except the water, which is usually introduced as a spray or mist. The reaction takes a certain time, as the nitrogen compounds which serve as carriers of oxygen have to be frequently reduced and reoxidised, and the gases and liquids take some considerable time to mix sufficiently intimately for their reaction.) According to the calculations given on p. 459, Vol. I, for each kilogram of sulphur in the form of brimstone 6199 l. of gas, or in the form of pyrites 8145 l. of gas, at 0° and 760 mm. pressure, must enter into reaction; and these figures are considerably increased by the higher temperature. (In order to deal with such vast quantities of gas, very large surfaces or spaces must be provided. Since the strongest acids have to be dealt with, both in the liquid and the gaseous form, most materials commonly used in building are out of the question; and since glass, earthenware, etc.,

are excluded by the large size of the apparatus, practically only *one* material remains which is sufficiently cheap and suitable for the purpose, namely, *lead*. The disadvantages of this metal, such as its great weight, its softness and lack of rigidity, its low fusing-point, and its comparatively high price, cannot outweigh the advantages which none of the base metals share with it for this purpose. These advantages are its great chemical resistance to the acid gases and liquids; its ductility, which permits rolling it into large sheets; its extraordinary pliability and toughness, in consequence of which it can be easily shaped in every possible way; and, lastly, even its easy fusibility, which permits the edges of two sheets to be so completely united by melting together with a strip of lead, that they form a whole for all practical purposes, and thus render it possible to make vessels of indefinitely large size and any shape, provided care be taken to support the walls of the vessel on the outside, lest they collapse by their own weight.

A special advantage of lead is that even after a number of years, when the chambers have become quite worn out, the greater portion of its value can be recovered by melting the material; even the mud containing lead can be utilised.

Sulphuric-acid Chambers from other Materials than Lead.—To this class belongs the proposal of Leyland and Deacon (British patents of 10th September and 2nd December 1853) to make them of hard-burnt firebricks, slate, sandstone, basalt, etc., set with a mixture of melted sulphur and sand.

General Notes on the Erection of Lead-chambers.

The chambers are always placed at some elevation above the ground level—at least, sufficiently high to allow a free passage underneath; more often they are much higher than this. The first object of this is to give the opportunity of ascertaining whether the chambers are tight. If their bottoms are not easily accessible, large quantities of sulphuric acid may be lost before a leak is detected. This means not merely a loss of acid, but that the foundations are corroded and undermined and the whole structure may collapse. The expense of building the chambers on pillars, etc., is not thrown away, as the whole space underneath, which has always a moderately

high temperature, can be used as a warehouse; or it may even, if high enough, be utilised for the pyrites-kilns, etc., although this course is not to be recommended. In the latter case the chambers should be from 17 to 20 ft. above the ground. At some works, which are pressed for space, even the saltcake-furnaces, ball-furnaces, etc., are built underneath the chambers.

In any case, the soil must first be examined to ascertain whether it affords a safe *foundation*; for if the soil settles more in one place than in another, the chamber gets out of plumb and its bottom out of level, which, owing to the acid lying on the bottom and to the instability of the chamber-sides, causes great inconvenience. (A rocky or pebbly ground is best; next to this, sand or clay.) Marl and limestone are bad, because sometimes acid will run over accidentally and act upon the ground; and this may happen even with clayey soil. In these cases, the whole soil underneath the chambers must be protected by a layer of asphalt.

The pillars upon which the chamber is erected must, of course, go down to the "rock" as in any ordinary building of considerable height. If the accumulation of made ground or loose earth is so deep that it would be too costly to excavate and raise the pillars from below, piles must be driven in, according to well-known building rules, and the pillars built upon these.

The *pillars* themselves can be made of brickwork, stone, cast iron, reinforced concrete, or wood. Sometimes, instead of single pillars, two longitudinal walls are erected, connected by cross joists and interrupted by doors, windows, etc.

Such long walls require much material, and make the space underneath the chambers dark, in spite of the windows. They are only suitable where the chambers are placed unusually high in order to build furnaces underneath. Up to a height of about 26 ft. metal pillars seem preferable.

The cheapest pillars are those made of wood or bricks; occasionally they are made of stone—much more frequently of iron or steel. If made of *wood*, round or canted balks of at least 10 in. (better 12 in.) thickness must be employed. Fir- or pine-wood is generally used, especially Scotch fir; but the American pitch-pine or yellow-pine, such as is used for ship-

building, is preferable (on account of its much greater durability) in spite of its higher price. This applies not merely to the pillars, but even more to the frame of the chamber itself. The pillars must vary in their thickness, mutual distance, and the way in which they are stayed, according to their height and the weight resting upon them (which may be taken at 150 lb. per superficial foot of the total chamber-area, for the lead, timber, and acid, the latter alone in a full chamber amounting to 120 lb. per superficial foot); but for an average height of 10 to 13 ft., which will not often be exceeded with wooden pillars, they ought not to be further apart than 10 to at most 13 ft. from centre to centre. They are put into stone sockets projecting from the ground. This prevents the bottom of the pillar being damaged by moisture or acid. The stone has at the top a hollow of $\frac{1}{2}$ to 1 in. depth, into which the foot of the pillar fits exactly, and into which a little tar is first of all poured. Wooden pillars do not last for any great length of time; they have not proved very trustworthy, and are rarely found now in larger works, at any rate as principal pillars, except where wood is very cheap.

Frequently *brick pillars* are employed. These also are not often made above 17 ft. high. Their horizontal section should be at least 18 in. (better 2 ft.) square. They are made of common bricks, with a mortar very poor in lime.

The brick pillars in many works have been replaced by cast-iron ones, because the former are not very durable, especially at the top, where the beams rest. Even the bricks themselves rot by contact with the acid. They stand better if previously soaked in hot tar, but they take the mortar very badly after such treatment. They may also be painted with hot tar afterwards.

On the Continent, where, in consequence of the colder winters and hotter summers, the chambers have to be placed in a closed building, the pillars may be built in with the main walls of this building; but it is preferable to keep them separate, as they settle down differently from the main walls.

Chambers 20 ft. and upwards in width are sometimes built with mixed pillars—viz., brick pillars for the two long sides, and wooden pillars for the centre row.

Stone pillars are not often used for acid-chambers. Made

of rough stones they would be extremely clumsy, and hewn stone in most places is too dear. On the other hand, of course, stone pillars of the latter kind are very substantial, and last almost for ever, unless the stone be very soft.

In the larger works in England *cast-iron* pillars are almost exclusively employed, in spite of their higher cost. These can be made 30 or even 36 ft. high; they take very little space, and are almost imperishable if painted from time to time. They can be weighted a good deal more than any other pillars, unless these are made very thick, and they can be used as supports for many other purposes by means of cast-on brackets or even of pieces bolted on subsequently. A solid foundation must be provided.

The cast-metal columns are now frequently made of an H-section gradually tapering upwards. Fig. 1 shows this more distinctly, together with a bracket on each side for receiving a wooden stay for the timber above. Another cross-shaped section is shown in Fig. 2. These constructions are better adapted for brackets, etc., than round columns. If higher than shown here (15 ft.), they must be correspondingly stronger—for instance, for 20 or 24 ft. height, 12 in. diameter at the base. Columns of this type can be placed at 20 ft. distance from centre to centre, if the beams resting upon them are strong enough.

Sometimes the columns are made of rolled-steel joists of H-section, with

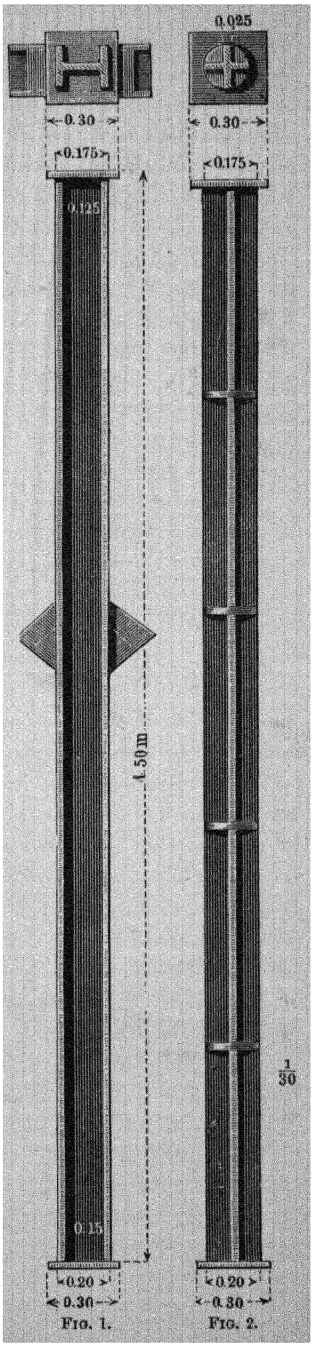


FIG. 1. FIG. 2.

the usual cappings and base plates attached ; these are much more reliable than cast iron.

The pillars are in most works placed so that they stand directly under the side frame, which has to carry the weight of the chamber-sides, and, in the English system, the whole weight of the chamber-top also. This, however, suffices only for very narrow chambers ; for chambers of ordinary width (from 20 ft. upwards) a centre row of pillars must be added to prevent sagging of the joints. As, however, the weight of the acid in a full chamber may be up to four times as much as that of the frame and lead combined, it seems more rational to place more pillars inside. Where steel joists are used for the beams, however, there is no need for the centre pillars.

Above the pillars there are generally placed *longitudinal sleepers*. If there is a continuous wall in place of pillars, it will be sufficient to cover this with a 2-in. plank ; but if there are separate pillars, the sleepers must be strong enough to support the whole structure of the chambers, both wood and lead, and their strength will then depend on the distance between the pillars. With chambers of 20 ft. height, and distances between the pillars of 20 ft. from centre to centre, the longitudinal sleepers should not be less than 12 to 14 in. deep by 6 in. wide, and ought, also, to be supported by stays, as shown in Fig. 3. With the pillars placed at shorter distances (say 10 to 13 ft.), timber of 6 by 12 in., on edge, suffices for the longitudinal sleepers. The joints of the beams of which they consist ought to be well connected, as shown, and should be placed between the pillars, where they are supported from below by the stays. The upper face of the sleepers must be levelled as well as possible from one end of the chambers to the other. Above these the *cross joists* are placed, running from side to side, and made long enough to carry the side frames.

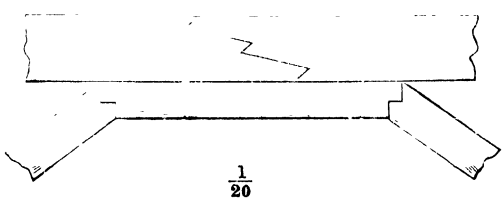


FIG. 3.

The horizontal distance of the floor-joists is usually 12 in. from centre to centre. Some works employ joists of 3 by

11 in. The length of the joists is equal to the width of the chambers *plus* the chamber-frame, *plus* the width of the passage.

The joists are covered with a $1\frac{1}{4}$-in. *floor*, laid quite level in all directions. As the flooring-boards are apt to warp in course of time from the heat of the chambers, this possibility must be prevented by nailing firmly down and punching down the heads of the nails. The importance of this precaution will be realised when it is remembered that this floor comes in direct contact with the soft lead.

On this floor the *frame of the chamber* is erected, which serves for supporting the lead. If constructed of *wood*, it consists, for each side of the chamber, of a sole-tree (sill) and a crown-tree (capping), connected by uprights or "standards," and further tied by cross rails or stays. The sole- and crown-trees and the corner uprights are of 6 in. square section for a chamber up to 20 ft. high; the remaining uprights are of 6 in. by 4 in. section, and they are mortised into the "trees." In the corners the trees project over and are rabbeted into each other. If no cross rails are employed, the uprights are placed 3 ft. 3 in. apart from each other; if they are connected by cross rails, they can be placed 4 ft. apart. The cross rails are 3 in. by $4\frac{1}{2}$ in.; they are only partly let into the uprights, in order not to weaken these, and are placed at vertical distances of 4 to 5 ft. from each other. The chamber-lead is kept a little away from the woodwork in order to expose the lead everywhere to the cooling action of the air. If this is not done, the lead is found to be quickly corroded in the parts protected against radiation of heat by the wood. It is now usual to shape the woodwork so as to present the least possible contact with the lead, as shown in Figs. 4 and 5. Practically the same effect is obtained by using round timber for uprights.

FIG. 4.

FIG. 5.

The best kind of timber for this purpose, as well as for all others where acids are concerned, is American yellow-pine or pitch-pine; but as this is frequently too expensive, ordinary red-wood is also very much in use. It is beneficial to protect it against the action of the acids by a coating of lime-wash,

which is at the same time a slight protection against the risk of fire. Another kind of protection from acids, although not from fire, consists in painting the woodwork with coal-tar, or preferably with a sort of tar-varnish, made by dissolving coal-tar pitch in heavy tar-oils, and known as "prepared" or "refined" tar.[1] This enters better into all the pores of the wood, and on drying does not leave so many crevices; it is altogether preferable to raw coal-tar for painting wood, iron, or brickwork, and is not much dearer.

The painting of the woodwork should be done twice, and before the lead is put on, so that all parts can be reached by the brush.

Special care must be taken lest any acid gets into the mortise-holes, where the uprights are joined to the sole-trees, etc. No empty space should be left where any acid could lodge, but all interstices should be filled up with coal-tar pitch or the like.

In France sometimes the bottoms of the uprights are not mortised into the sole-tree, but rest flatly upon them, being kept in place by pressure and friction only.

Whether cross rails are used or not, in any case there should be diagonal stays, to give more stability to the frame. It is not of much consequence how the stays are put, so long as this is done according to the well-known rules of carpentry.

If, as is usual in England, the chambers are placed in the open air, one side of the frame is made about a foot higher than the other, so that the rain-water and melted snow can run off, and on the lower side a water-spout is arranged so

[1] Cresse, *Chem. and Met. Eng.*, **26** (3), 111 (1922), mentions that the beetle Capicorn, more commonly known as the Goat beetle or Sawyer worm, or, technically, as the *Monohammus confusor*, causes much destruction in some varieties of wood. Starting as an egg laid by the female on the surface of the timber, it hatches into a borer. It feeds on the sapwood, weaving back and forth until grown to full size, when it mines deep into the heartwood and back to the surface again. Here it passes through a resting-stage and is transformed into a long-horned beetle. When it mines the timber and meets with the lead lining, it proceeds to feed on the lead.

The action of these beetles causing leaks in acid tanks and chambers has been known for years. Timber liable to be attacked by these pests should be creosoted.

that the rain-water cannot run along the chamber-side into the acid at the bottom.

Nowadays the chamber-frames are made of *angle-iron*. This plan has the advantage of presenting an extremely durable and clean erection and of avoiding overheating of the lead in any part. No nails are employed at all; the lead straps are simply bent round the angle-irons, or clamped between two angle-iron uprights. The roof is suspended from angle-irons in exactly the same way. Of course, iron frames are more costly than wooden, and must be kept in order by painting from time to time, preferably with coal-tar varnish.

Lead for Chambers.

The chamber is made of sheet-lead as wide as the rolling-mills can supply it, and of convenient length, so as to have as few seams as possible. The usual *thickness* in England is 6 lb. to the superficial foot, sometimes 7 lb., especially for the ends and the top, or for the first chamber of a set.

This thickness is sufficient for a chamber to last upwards of ten years; the bottom lasts longest, because it does not get so hot as the sides and the top, and it is also more protected by the mud of lead sulphate which collects upon it; only in cases of gross neglect (for instance, if nitric acid gets to it) is it quickly worn out, whether the lead be thick or thin. Where *zinc-blende* is used, the *mercury* contained in it may have a different effect, especially since the blende-furnaces are driven at a higher temperature, so that more mercury gets into the chambers. According to information received from Hasenclever in 1902, it has been noticed at Stolberg that the mercury acts most strongly at the lateral parts of the bottom, which are less protected by the sulphate-of-lead mud, and where the joint between the side sheet and the bottom sheet causes the double layer of lead to collect acid and mercury between the two sheets. Here sometimes mercury is visible in globules, and that part is worn out in less than three years. Hence the whole bottom is made of stronger lead, rolled extra strong at the part next to the sides, which is, moreover, protected by a covering of acid-proof flags. (*Cf.* p. 131, Vol. I.)

At some of the best English works, 7-lb. lead is used

throughout for the chambers, and in the most exposed places, such as the front and back ends of the leading-chamber and several feet of the sides adjoining these, 9-lb. is used. Sometimes the side sheets are rolled so that the upper and lower two feet are made stronger than the remainder, because these parts are more quickly worn out. Chambers built in this careful way last upwards of twenty years.

The *quality* of the lead is of great importance, and as this subject has already been fully discussed (see p. 224 of Vol. I) it need not be repeated here.

Joining the Lead Sheets.—The sheets of lead were, in the infancy of acid-making, joined together by the ordinary *soft solder*, which is very convenient for use, but is soon corroded by the acid. Places soldered thus are also much more brittle than pure lead. So long as the chambers had to be put together in this way, innumerable repairs were necessary.

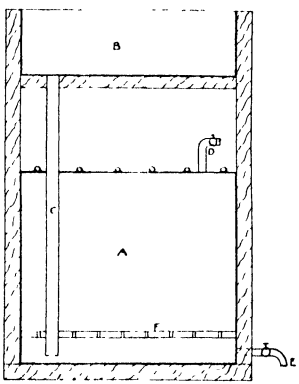


FIG. 6.

The kind of joint now generally employed is that made by *burning*, employing the lead itself as solder—that is, by melting it with a hydrogen or other non-luminous flame fed by compressed air. In this way the two sheets are joined so tightly, that with good work the joint, being thicker than the sheets, is actually stronger than the latter. If the joint is rough and uneven, foreign substances will easily be deposited in the rough parts, by which the lead may be damaged.

E. von Lippmann[1] has shown that the process of burning lead was known in the Middle Ages, and perhaps in ancient times.

The apparatus known as the "plumber's machine" is shown in Fig. 6, and is usually constructed of wood lined with lead.

A contains the grating F, upon which the granulated or scrap zinc is placed. The upper compartment B contains the

[1] *Chem. Zeit.*, 1812, p. 437.

dilute sulphuric acid,[1] with the connection C, for the acid to flow to the lower one. The connection D, which is provided with a tap, is the gas exit. E is a run-off for the resultant sulphate of zinc.

The second part of the apparatus is simply a portable bellows of cylindrical shape, the lever of which a boy works with his foot. Elastic tubes are connected, one to the hydrogen apparatus and the other to the bellows, and joined to a blowpipe, Fig. 7; and the mixture is ignited. Each limb of the blowpipe is provided with a stopcock. By turning these the plumber may admit more air or hydrogen at will, and thus can produce a flame of any size, which, however, must never be an oxidising one. The art of burning consists in touching and melting parts of two sheets *at the same time*, which, on cooling, solidify to a whole.

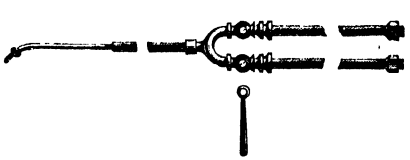


FIG. 7.

Lead-burning is work requiring much practice, because the plumber must not allow the flame to act a moment too short or too long, and none but experienced workmen should be employed. Wherever it is possible, one sheet is laid about 2 in. over the edge of the other, as shown in Fig. 8, and the seam made with the help of a strip of pure lead.

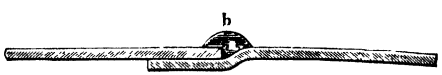


FIG. 8.

The burning of *perpendicular* (upright) joints is difficult, and, even in the hands of the most experienced workmen, takes longer for the same length of seam than horizontal burning, without ever being as strong as the latter. This is easily understood. The melted lead, which remains lying on a horizontal sheet, in upright burning at once runs down. This can be prevented only in one way. The lead must be heated exactly up to the melting-point, and the flame instantly removed till the seam has solidified. The burning must always be done

[1] Hydrochloric acid, in the place of sulphuric acid, cannot be employed in the plumber's machine, as it cannot be left in prolonged contact with lead, and it is also contended that the workmen are injured by the hydrogen made by means of hydrochloric acid.

from the bottom upwards, so that, to a certain extent, the seam will retain the drops of lead.

It is usual to avoid perpendicular burning as far as possible by burning as much as can be lifted safely.

The work is dangerous when materials containing arsenic are employed. Arsenic may be present in the hydrogen, as AsH_3, and the safest way of removing it is by proper washing of the gas, this being done by a 5 per cent. solution of potassium permanganate, which is more efficient than cupric sulphate.

The several gases used by the up-to-date plumber, such as hydrogen, oxygen, coal-gas (and even air), can now be obtained in steel cylinders provided with suitable regulating taps or valves and containing 20 to 100 cub. ft. and upwards. They are quite portable, and, in the hands of a workman of ordinary intelligence, safe to use.

The use of compressed hydrogen not merely prevents any danger from arsenic, but is also very much cheaper than the evolution from zinc and sulphuric acid. The hydrogen is burned without having recourse to compressed air, by means of special burners.

The way of erecting a lead-chamber in England is usually as follows:—The commencement is made with the sides, for which the sheets are obtained as wide as possible (most lead-rolling mills supply them up to 9 ft., some even wider), and long enough to extend beyond the height of the chamber, taking into account the fact that one side of the chamber is a foot higher than the other. Six inches are required to turn over the crown-tree; but 2 in. are saved at the bottom, because the lead afterwards expands by the heat of the chamber.

On the wooden floor previously mentioned, a wooden table (the "sheet-board") is then constructed. This is held together at the back by battens, and is made quite smooth on the upper surface. It has the width of two or three sheets of lead, and a length equal to the height of the chamber. This, of course, can only be done when (as is generally the case) the chamber is at least as wide as it is high. On this table the sheets of lead are rolled out flat, placed side by side, so that one overlaps the other by 2 in., and burned together. At the same time all the straps (of which mention will be made later) are

burnt to the lead, which can be done because the upper surface will afterwards be the outer one. The upper edge is bent round the sheet-board so as to hold it fast, and when everything is finished this end is wound up by a set of pulleys, so that the sheet-board is raised together with the sheets of lead and lies flat against one side of the chamber-frame. The upper edge of the lead is then bent over the crown-tree and nailed down, the straps being nailed down also. For this purpose no cut or wire nails must be used; wrought-iron nails with broad heads ("clout-nails"), about 1½ in. long, are the best, the heads being protected against the acid by dipping them into molten lead. When the lead has been completely fastened to the frame the sheet-board is lowered down, moved forward its own width, and another piece of the chamber-side made upon it, till in this way the chamber-sides and ends have all been finished. It is preferable to use a single sheet bent to form a rounded corner, as this is stronger than the square corner formed by joining two sheets. The object of the process described above is to reduce the upright burning to a minimum. It is much better than the former plan of hoisting up each single sheet, turning its margin over the crown-tree, and unrolling the sheet by its own weight. In this case every single sheet had to be joined to its neighbour by upright burning, and the straps had to be burnt on in an equally inconvenient manner. If at all possible, the seams ought not to be behind the uprights, so as to be better accessible for repairs; and for this reason also, it is recommended to make the chamber-frame as shown in Figs. 4, 5, or 12, where the uprights do not touch the lead at all.

The *straps of the sides* must be arranged according to the style of the frame. If this consists only of uprights mortised into the crown- and sole-trees, without any cross rails, the straps are made of perpendicular pieces of lead nailed sideways to the uprights with leaded nails, and should be long enough to turn over the edge of the upright, so that two of the nails come to the front (Fig. 9, upper part). The straps are placed alternately on one and on the other side of the upright, one about every 4 ft. These nailed straps prevent the chamber-lead from following the changes of temperature by expansion or contraction, which may lead to deformation of the sides and tearing

off of the straps. It is therefore better to avoid this possibility by nailing down only the top strap. Instead of the lower straps, longer pieces of lead are burnt to the chamber-side on each side of the upright, which meet on its front and are there joined by rabbeting (*see* Fig. 9, lower part, and Fig. 10).

No nails are used here, so that the lead walls may move up and down the upright, whilst at the same time they are all the more stiffened by being held fast in two places. Fastening the lead-sheets to the uprights in this manner, of course, takes

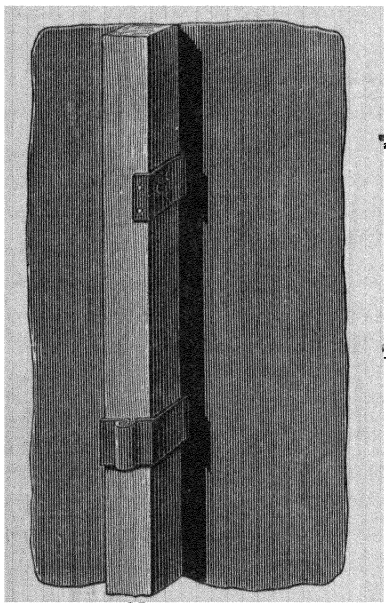


FIG. 9.

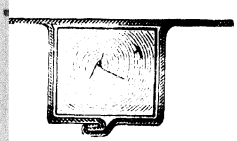


FIG. 10.

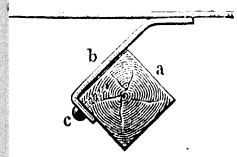


FIG. 11.

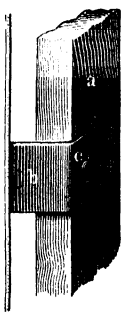


FIG. 12.

more lead and labour than simple straps. In each case the straps are about 8 in. in depth.

The object of keeping the lead clear of the wood, and of giving it scope for expanding, is well attained in the form of strap shown in Figs. 11 and 12. The upright *a* is placed with one of its edges pointing towards the chamber. The strap *b* turns round the edge of *a*, and is fastened to it, not by ordinary nails, but by a broad-headed pin *c*, which passes through a slit 2 in. in height. This arrangement allows the strap to work up and down as the chamber-side expands and contracts.

If the frame is provided with horizontal cross rails, only a

few upright straps are used—sometimes only horizontal straps. These are turned down over the rail, and nailed to it (Fig. 13), two of 6 in. length for each rail. The horizontal straps protect the chamber-sides much better against deformation than the upright straps, and carry the weight better upon the frame; they also permit the lead to be kept further apart from the wood, since the straps may leave about ½ in. (not more) space between the lead and the rails. The drawing shows this.

The chamber-sides can also be made of horizontally disposed sheets of lead. The overlap in this case is nailed

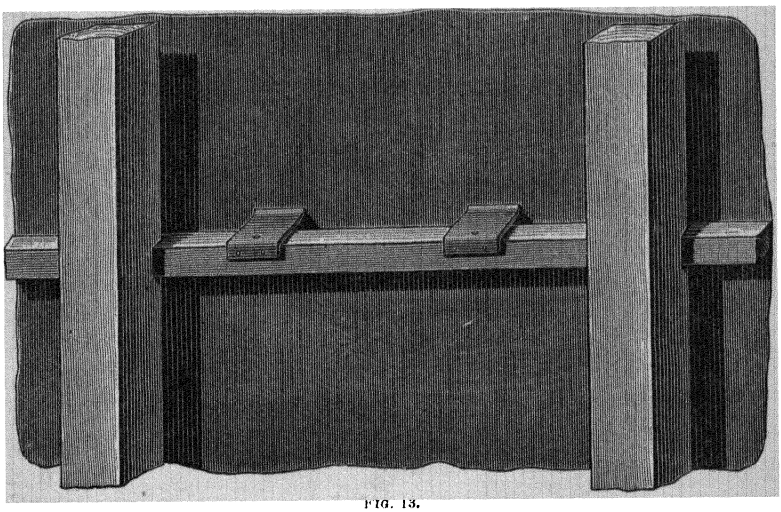


FIG. 13.

to the horizontal cross rails in lieu of straps, as shown in Fig. 14.

In this way there is not so much pull upon the seams as if the chamber were made of sheets hanging down by their length, since each sheet is supported just in the place where there is most strain. This plan, indeed, seems to be worthy of general adoption; for it saves the lead and labour of all the straps, and supports the chamber very well.

The plan used at Aussig is equally substantial. There are no side-straps at all, but for each upright of the frame there is a strip of lead burnt to the chamber-side along its whole height, the lap being turned outside. This is nailed sideways

to the upright. Between this and the lead there is a wooden lath, to increase the contact of air with the chamber-lead as much as possible. Fig. 15 shows this in horizontal section.

Benker ascribes great advantages to his *perforated straps*, shown in Figs. 16 to 18. Fig. 16 is a plan showing the chamber-side *a*, the uprights *b*, the cross-bars *c*, the small wooden bars *d*, and the straps *e*. The same parts are seen in vertical section in Fig. 17. The chamber-lead is kept 2 or 2½ in. apart from the cross-bars; the perforations of the straps (which may extend the whole width of the cross-bars, as in Fig. 18) cause a strong current of air to rise upwards and cool the lead, without allowing any quantity of dust to accumulate on the straps. This system is especially recommended for chambers which are driven hard for the "high-pressure style" of work (*v. infra*).

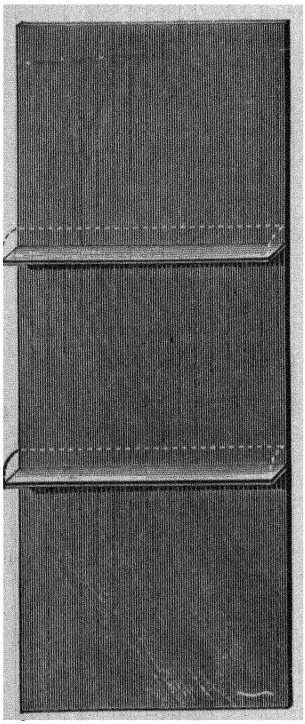


FIG. 14.

The present practice in England is, first, to burn the seams from the top down for about a yard only, so that the chamber can be covered in. The remainder is then done at leisure in bad weather. The next thing, therefore, is the *chamber-top*.

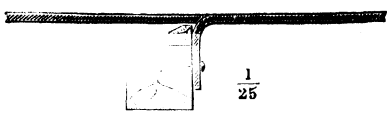


FIG. 15.

For this a temporary scaffolding is required, movable on wooden rollers, made of high trestles joined together at the top, equal in height and width to the chamber, and in length to at least two (or, better, three) sheets of lead. It is covered on the top with a flooring of boards; and upon this the sheets serving for the chamber-top are laid. These are a little longer than the width of the chamber, so that they project 3 in. on each side. Thus they do not project quite so far as the

overlap of the side sheets (6 in.), and there remains a joint suitable for burning, which is made very strong. The sheets themselves are then joined by burning, and all the top straps

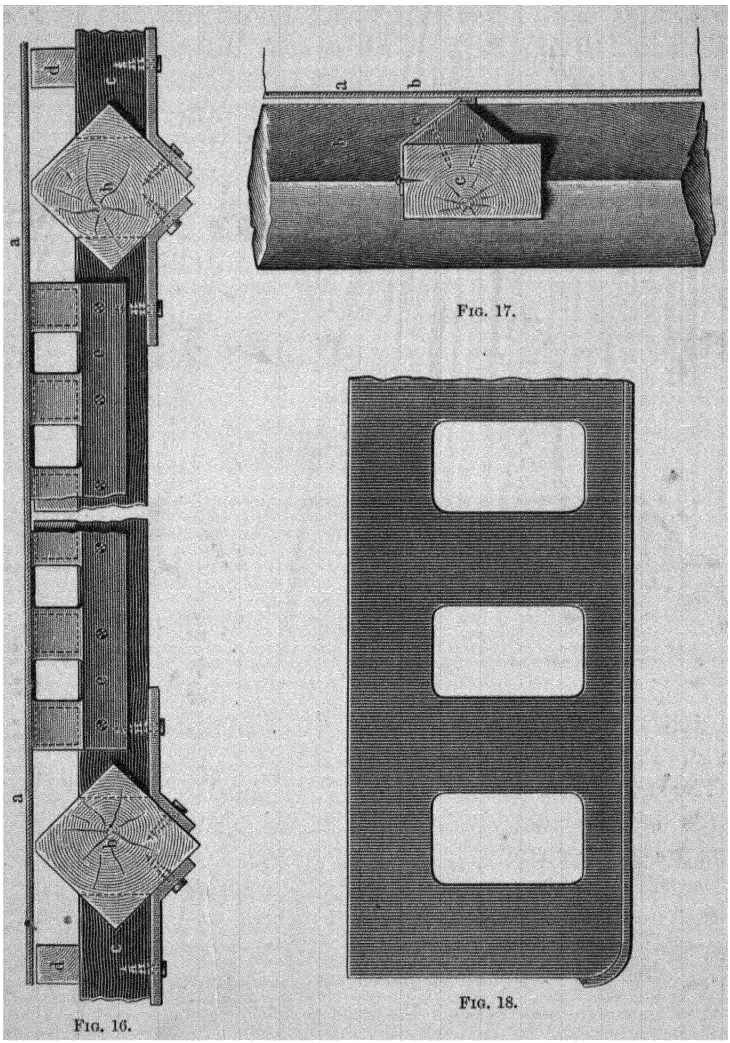


FIG. 16.

FIG. 17.

FIG. 18.

are burnt on. These, in England, serve for fixing the chamber-top from above to the top joists carrying it. The latter, for a chamber 20 to 26 ft. wide, are 3 to 4 in. thick and 10 to 12 in. high, and are placed at 14 to 15 in. centres. Their

length should be at least sufficient to reach to the outside of the crown-trees; it is better if they even project a little beyond, to have a good support. The straps themselves are made 7 in. square (or triangular), and stand alternately on both sides of the top joists, about 3 ft. apart on each side. At some works there are fewer but longer straps. They are bent up and nailed to the top joists, laid above them on edge, with leaded nails. When all this has been done, the top joists, by the help of the straps, carry the lead of the chamber-top, and the joists themselves rest upon the side frames, but separated from them by the overlap of the chamber-sides.

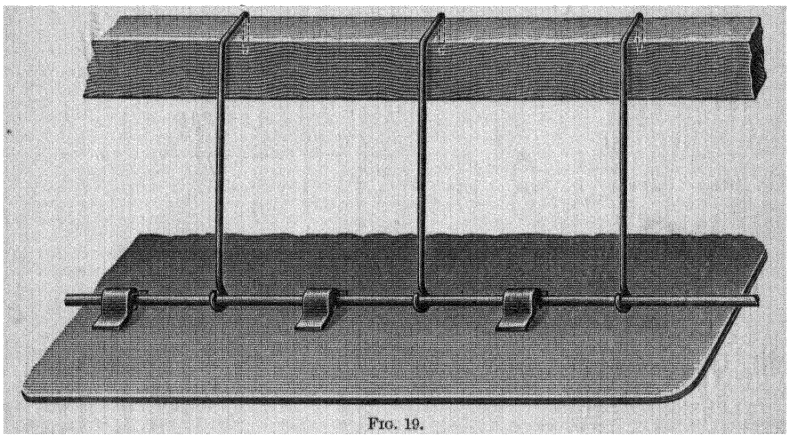


FIG. 19.

The joists should be well clear of the chamber-top, so that air can circulate between lead and wood.

The top joists are prevented from canting over by a few boards nailed across them, which at the same time serve as a passage on the chamber-top. Where the chambers are roofed in, longitudinal sleepers are sometimes laid on the top, joined to the top joists by iron clamps, and the whole is suspended from the timber of the roof, which must be made strong enough for this purpose; but it should not be overlooked that, even in the case of roofed-in chambers, it is safer to keep the chamber-top independent of any movement of the roof.

In some cases there are no wooden top joists, but, in place of these, iron rods about $\frac{1}{2}$ in. thick, fastened to the chamber-top by lead straps burnt on each side to the chamber-lead. These horizontal rods are suspended from the roofing by

means of ¼-in. rods placed at short distances from each other. This system cannot be employed for chambers standing in the open air, as it makes the chamber-top dependent upon the beams of the roof; it is shown in Fig. 19.

The *chamber-bottom* is made last of all, but not always in the same way. In some works, the side sheets are burned to it all round, and openings are left for drawing off the acid,

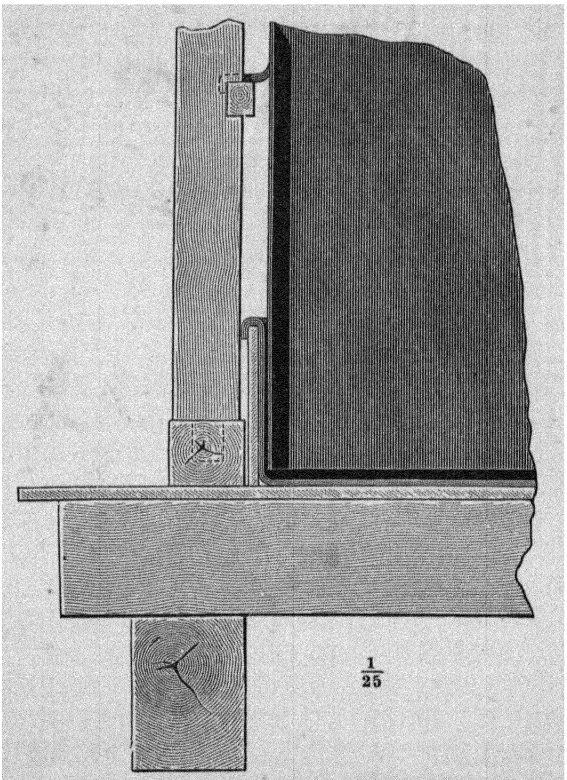


FIG. 20.

for taking samples, etc. In the majority of works, the bottom is independent of the sides, and forms a tank with turned-up sides, into which the chamber-sides hang down, dipping into the bottom-acid, and thus forming a hydraulic seal. This allows the chamber-sides to expand and contract with the temperature, and also makes the bottom-acid accessible from all sides, so that it is generally preferred in spite of the larger

expenditure of lead. A good many works, however, have adopted the first-mentioned plan of making the chamber as a closed box, which saves both lead and the trouble unavoidably connected with the second system. Often the upstand, which should be 20 in. to 30 in. high, so as to afford a good deal of room for acid, is made from a narrow sheet of lead of double width, by bending up one half and leaving the other half to form a portion of the chamber-bottom; the latter is then finished by burning it together with other sheets of lead. This is more convenient for the plumber than taking sheets equal in length to the width of the chamber, *plus* the height of the upstand on each side. The upstand must not be left loose, because it would be easily deformed by the side pressure of the acid. To prevent this, a 1½ in. board is placed all round the chamber-floor, over the edge of which the upstand is turned and nailed down. This is shown in Fig. 20. Instead of a solid board, it is preferable to employ merely a number of perpendicular or horizontal rails, which permit the cooling action of the air upon the lead.

Some manufacturers construct the upstand with 20-lb. lead, and claim a much longer life of the chamber as a whole.

Falding[1] gives details of chamber construction which refer to the usual English plan, which is generally followed in America as well. Fig. 21 shows parts of the chamber-side in elevation. The pillars (posts) *a a* are of 14 × 14 in. wood; corbels *b b*, 14 × 14 × 5 in.; stringers *c*, 14 × 14 in.; joists *d*, 3 × 15 in., 16 in. centre to centre, 3 × 2 in. herring-bone-strutting; gangway-floor *e*, with 2 × 12 in. joists. Of the chamber-frame itself, the sill *f* is 6 × 10 in., with a dowel-pin at each post and toe-nail to each intermediate upright. The strong uprights (posts) *g g*, 6 × 6 in., 13 ft. 9 in. from centre to centre; the intermediates *h h*, 6 × 2 in., 33 in. centres; the bracing *i i*, 6 × 2 in., with lag-screw to each post and spike to each intermediate. Crown-tree *k*, 6 × 10 in., with lag-screw at each post and toe-nail to each intermediate upright. Top joists *l l*, 3 × 15 in., 14 in. centres, with three lines of solid 2 × 12 in. board-bridging. Fig. 22 represents a portion of chamber-ceiling, seen from above, and Fig. 23 the same in sectional elevation on a larger scale, which clearly shows how

[1] *Min. Ind.*, 7, 679 *et seq.*

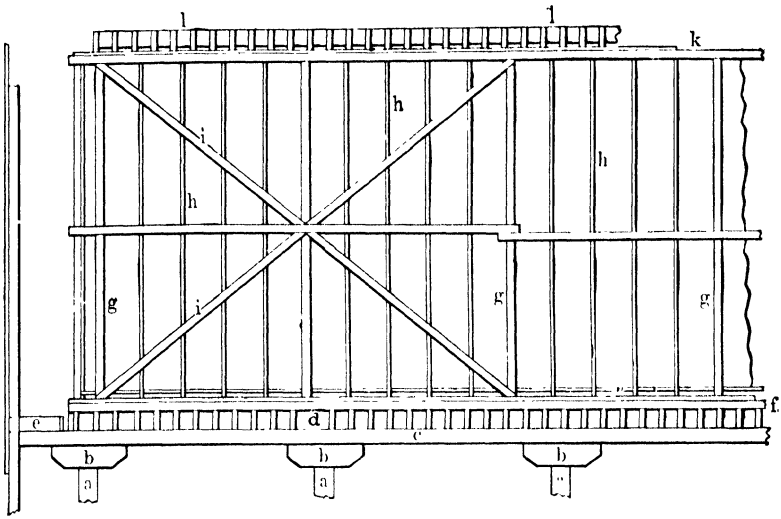


FIG. 21.

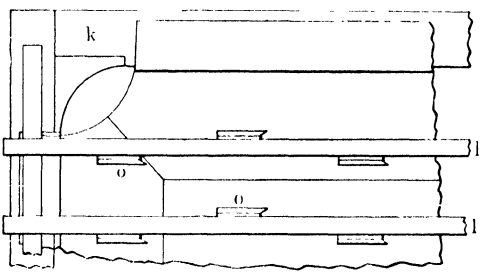


FIG. 22.

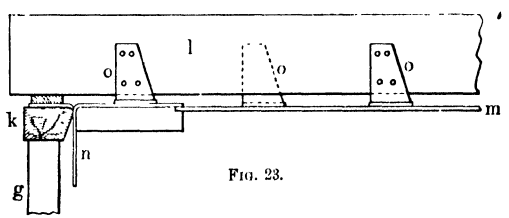


FIG. 23.

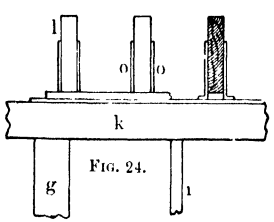


FIG. 24.

FIG 25.

the chamber-lead *m* at the top is joined to the sides *n*, and turned over the crown *k*, and how the straps *o o* (24 in. centre) suspend the top from joists *l l*. Fig. 24 makes this clearer by a side elevation, and Fig. 25 shows the way the straps are cut from a strip of rolled lead. Fig. 26 gives a plan-section of a chamber-corner, and Fig. 27 a sectional elevation of the lower part of a chamber, showing how the straps *r r* are fastened to the uprights *g*, *h*, and how the lead

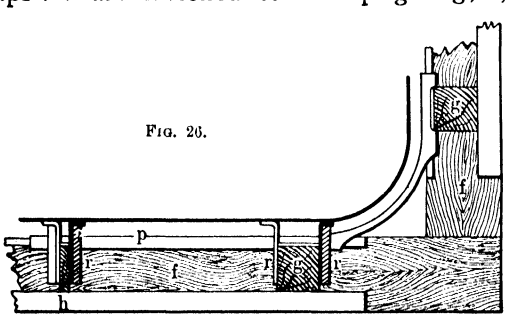


FIG. 26.

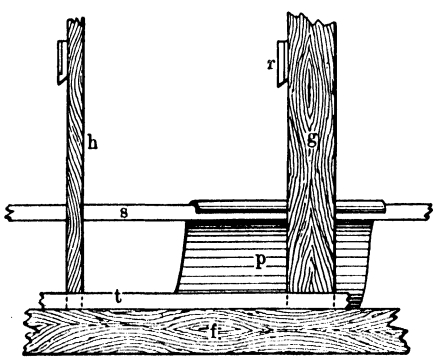


FIG. 28.

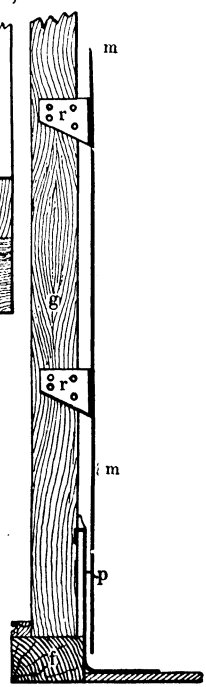


FIG. 27.

side *m* and the saucer *p* stand off. Lastly, Fig. 28 shows how the upstand *p* of the saucer is turned over ledge *s* (2 × 1 in.) and held at the bottom by another strip *t* (3 × 2 in.) fastened to the sill *f*.

Special Ways of building Chambers.

As the side walls of the chambers, in consequence of the variations of temperature, gradually change their form, Petersen and Ising (Ger. P. 218726) make them movable by suspending

them on bearings which can slide along the chamber-frame. This allows the changes caused by variations of temperature to take place without any deformation of the lead.

Guttmann [1] describes the way in which a chamber of 40 ft. height was built. Horizontal wooden beams are suspended by iron rods, and can be levelled by adjusting the nuts provided. The whole 40 ft. length of 6-lb. lead is suspended in two places only, in the following manner: An iron rod, $\frac{1}{2}$ in. diameter, is laid horizontally against the lead and held in place by straps. A double hook, made of $\frac{1}{4}$ in. round iron, grips the iron rod at one end, whilst the other end is hung on the wooden beam, where it is hammered flat and nailed down. The hooks are spaced 20 in. apart, so that only about 2 cwt. of lead are supported by each hook. This construction is both simple and cheap. The lead is free to expand, and the hooks being elastic there is no unequal strain, as is generally the case with straps. The side of the chamber hangs down practically like a curtain, and yields even to wind pressure, whilst it does not buckle. Such a chamber must be housed, as it would scarcely stand in the open, especially if exposed to strong winds.

Nemes (B. P. 24223 of 1913) strengthens both the sides and the bottom of the chambers by iron supports, arranged in such a way that any leakages occurring in the chamber-bottom, especially in the corners, are immediately discovered before they have corroded the iron. The lead straps for holding the chamber-sides surround the upright column of the iron framework, and rest upon projections provided on those columns. The lead chamber-bottom is not strengthened from without by sheet-iron, but rests on an iron framework attached to the columns, whereby the chamber-bottom is cooled and made accessible in all places. It rests upon a wooden floor, which allows any leakages of acid to be easily noticed.

Seeck (B. P. 16187 of 1914; Fr. P. 474502) suspends the lead sheets from flat iron rails, tubes, etc., resting freely on hooks suspended on bearers. The hooks may be placed at any desired height; they are at a right angle to the sheets of lead, and touch these only at one point.

The chambers constructed by Simon-Carves, Ltd., are on the Moritz system (B. P. 11123 of 1909; U.S. P. 981103;

[1] *J. Soc. Chem. Ind.*, 1908, p. 667.

F. P. 395694 ; and Ger. P. 235,800), which were introduced in

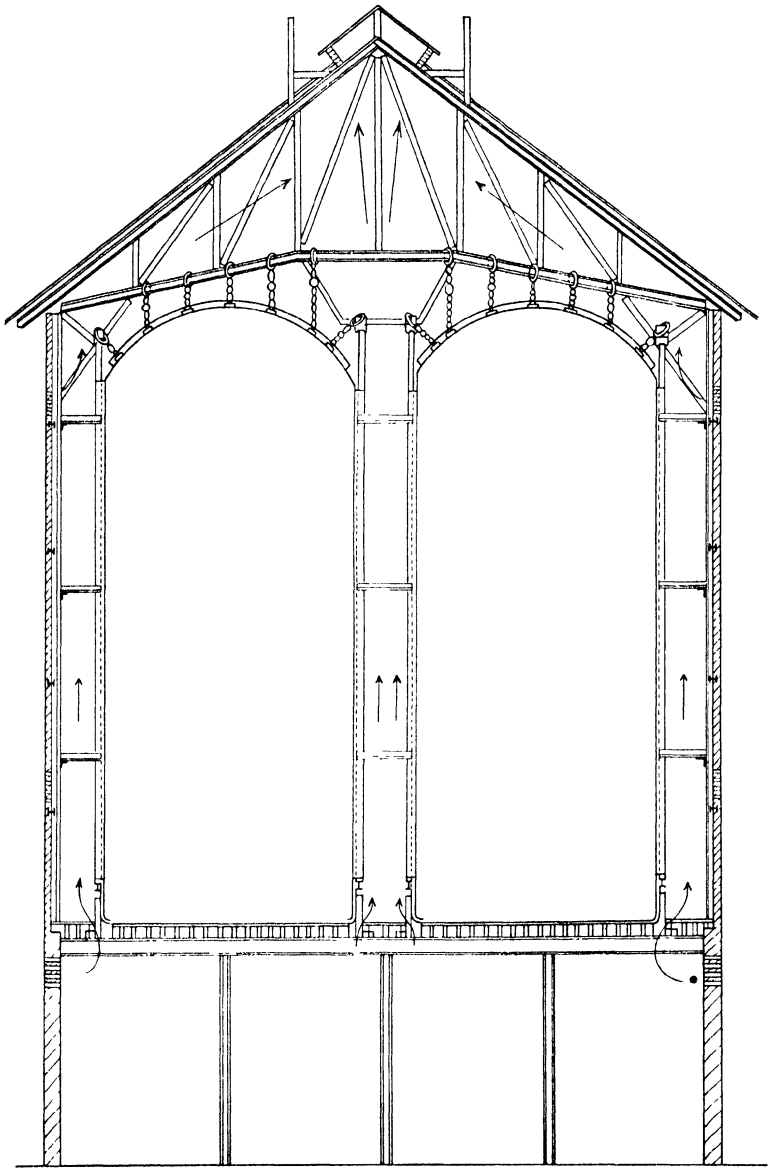


Fig. 28a.

Northern France by the Soc. anon. des Établ. Eyken et Leroy, and

later at other works in France and Belgium, and the "Union" Chemical Works at Elberfeld. The cross-section of the standard chamber is 18 ft. wide × 42 ft. to 45 ft. high, and the leadwork is vertically suspended, the arrangement being clearly shown in Fig. 28*a*. Flat steel bars, $1\frac{1}{2}$ in. × $\frac{1}{4}$ in. section, are sheathed with lead and burnt on to the side sheets

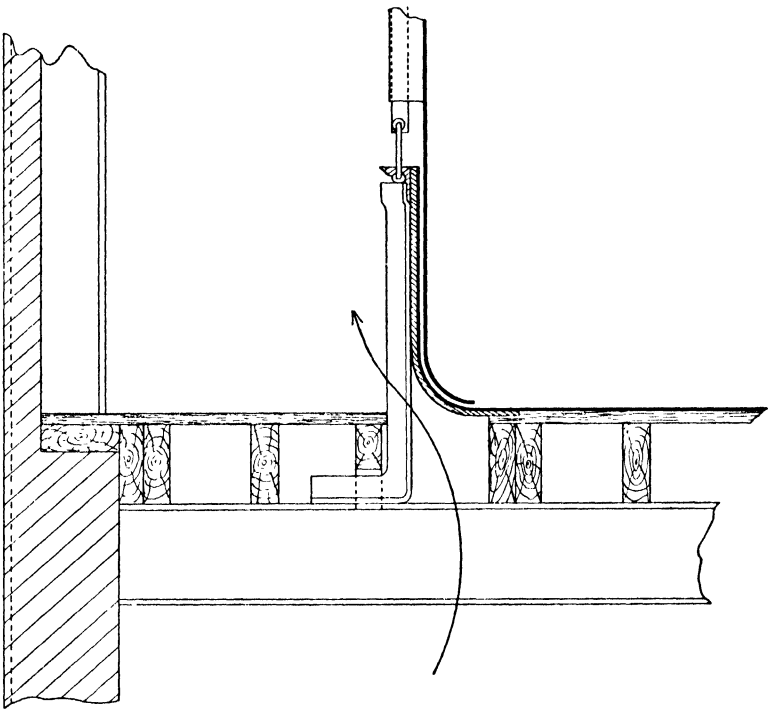


FIG. 28*b*.

of the chamber in a vertical position, and are slung by means of stirrups from an overhead gantry. The chambers are thus freely suspended and not rigidly held at any point.

The tops of the chambers are of segmental shape, in order to give increased strength, to assist circulation of the gases, and to prevent the lodgment of dust or water, which would interfere with radiation. The suspension of the tops is effected in a similar manner to that of the chamber-sides. Small steel flats of segmental shape are enclosed in lead, burnt to the roof, and suspended from the structure by means of twisted steel wires.

All suspensions are thus capable of adjustment, and the whole of the lead sides and tops present a free surface for radiation. It is claimed that the suspension strips or gills, which are spaced at about 2 ft. 6 in. intervals along the chamber, increase the radiation surface and thus assist the dispersion of heat.

The acid dish or upstand consists of a steel plate of "L" section with rounded corners, fixed upon a timber platform, which forms the bottom of the dish. The dish is completely lined with lead, and is provided at the top with angle-iron curb. In this curb each vertical suspension bar is anchored by means of a hook bolt to prevent excessive movement of the lead, which might occur in the event of undue suction being inadvertently formed in the chambers, due to neglect of the regulation of the exit fan. The timber floor upon which the dishes rest is arranged with an opening around the sides of the dishes to allow air to circulate around the outside of the steel sides, thus cooling the acid in the dishes. This is clearly shown in Fig. 28*b*.

The suspension bars of the chambers are slung from overhead girders connected by a series of ceiling joists, the girders being built in the form of a roof principal and supported upon steel joist columns. The skeleton steel framework so formed, is panelled out by means of horizontal joists and filled in with $4\frac{1}{2}$ in. brickwork walls, thus providing a substantial weatherproof building.

In the brick screen walls openings are provided for air currents to play upon the sides of the chambers, so that a considerable chimney effect is produced in the gangway space between the chambers, this space being about 4 ft. wide. The movement of cold air outside the chambers is not impeded by the suspension, as it is parallel with the bars, and a corresponding downward movement is given to the gases inside the chambers along the internal surface of the lead. This movement of the gases is also assisted by the segmental shape of the chamber-top, which permits of a very effective radiation of heat.

On account of the protection of the chambers by a weatherproof building, and the method of suspension, which allows the lead to expand without stress, and the absence of abrupt corners (all angles being radiused), the lead is not subject to

bending stresses and subsequent crystallisation as is the case where it is rigidly held to a fixed frame, and consequently the life of the lead is lengthened. The narrow and high section of the chambers promotes an intensified circulation of gases giving a greater rate of contact with the surface of the lead, and therefore the chamber volume required for a given production is materially reduced. A further feature of this construction is that the only timber employed is that for the floor, and even this can, if desired, be left out entirely and the whole of the work constructed in steel, thus eliminating fire risks. Also, owing to the height of the chambers and the smaller volume, the ground space occupied is materially reduced. The gas trunks between the chambers are of circular section and suspended by steel bars and bends, the gas entering near the top of the chamber and leaving near the bottom.

For normal working this type of chamber requires a volume of 7 to 8 cub. ft. per lb. of sulphur burnt per 24 hours, and the nitre consumption is said to be 1·6 per cent. on the sulphur consumed.

Kalinowsky (Ger. P. 260991) describes carrying-lashes firmly burnt to the chamber-walls, and fastened by means of hook screws on iron rods or tubes, in such a way that they can be moved and turned. The carrying rods or tubes are placed in beams provided with slots, in which they can be moved backwards and forwards.

E. Hartmann (formerly E. Hartmann and F. Benker, B. P. 17035 of 1913; Ger. P. 271926) fixes the lead sheets of vitriol chambers on horizontal rods, avoiding a special chamber-frame by suspending the lead sheets by means of rods, independently of the roof of the building, which can be done away with entirely. His specification runs as follows:—

The forms of iron chamber construction hitherto known, which allowed the suspension of the lead sides and top of vitriol chambers without a regular frame, were all dependent on the presence of a roof, as this was required for bearing all the arrangements for suspension. Circumstances may arise, however, which make it necessary or advisable to choose the form of the roof and its strength independently of the iron construction carrying the sheets of lead, or even to dispense altogether with a roof, as is usual in countries with a suitable

climate, without abandoning the advantage of a free suspension of the lead sheets—that is, without a chamber-frame in the ordinary sense. This is made possible by the construction shown in Fig. 29 (*a* to *d*). The lead sheets are supported by the trestles *a a*, in the shape of lattices, or in other ways,

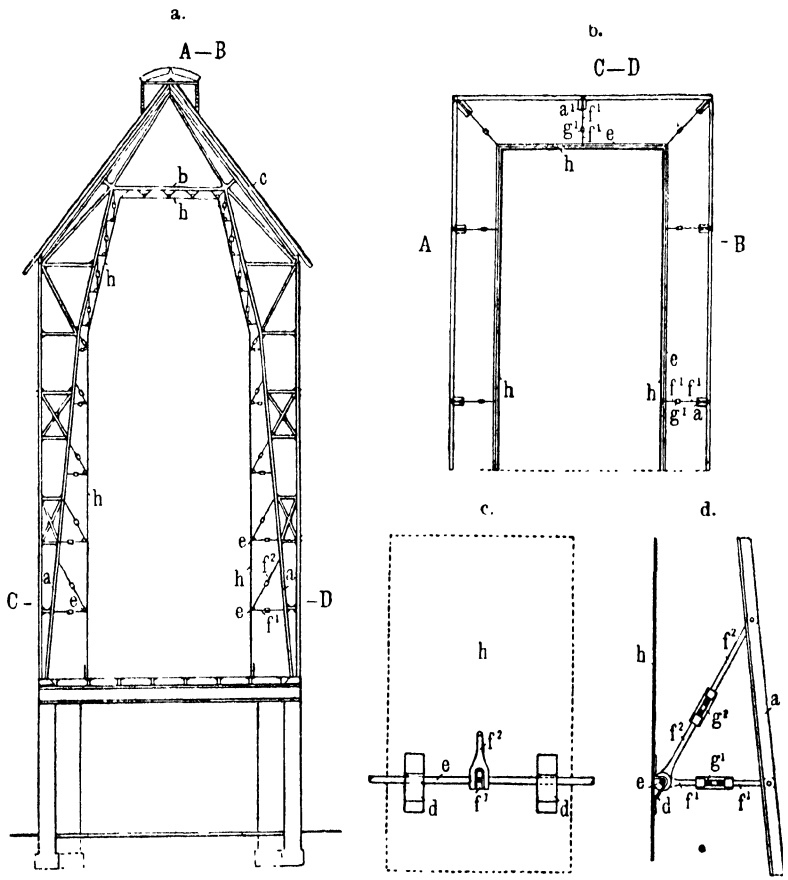


FIG. 29.

preferably made of iron ; but other materials, *e.g.* wood, may also be used. The trestles *a a* are kept in the proper position by stays *b b* at their upper side. The roof of the building, *c*, rests on the trestles, but it may be dispensed with altogether. The lead sheets of the chamber, *h h*, are provided with straps *d*, through which pass the horizontal rods *e*.

The Metallbank und Metallurgische Gesellschaft A.-G., of Frankfurt a.M., which has carried out that invention on a very large scale, points out that it makes it possible to build *high* chambers with all their advantages, and it also admits of repairing the lead sheets in any place, as they are accessible everywhere. If any of the iron suspending parts suffer damage, they may be replaced by new ones without any interruption of the work. The chamber-frame itself is kept away from the damaging influence of the sulphuric acid.

Harris and Thomas (B. P. 6026 of 1915) surround and support the chambers by vertical pillars and horizontal girders, the curtain being attached to the latter by means of hooks. Every hook is pivoted on a leaden strip fixed to the curtain, and its other end, shaped like a U, fits into a similarly shaped piece on the girder. A block is wedged in between the curtain and the framework at the point of attachment of the hook. A rent or tear in the curtain is readily accessible, as only one hook has to be detached. The roof is arched, and suspended by similar hooks from bars arranged radially between a central ring and the outer framework.

Ising (Ger. P. 267513) aims at preventing the rapid destruction of the chamber-walls by acid condensing upon them, which gets mixed with lead slime and runs down; this causes a rapid corrosion of the lead, which increases with the amount of acid running down and with the height of the chambers. It can be avoided or essentially lessened by arranging, inside the chambers, leaden ledges fastened to the sides by burning on, or otherwise, at certain distances. In a chamber 12 m. high, *e.g.*, the first ledge is provided 2 m., the second 4 m., from the top, and so forth at distances of 2 m. from one another, the lowest being 2 m. above the chamber-bottom. The ledges are moulded in such a way that the liquid collecting on them runs off into the bottom-acid, as shown in Fig. 30. They are made of such breadth that the acid collecting upon them can run down without touching the ledges below; in the case of five ledges, the top one has a breadth of 5 cm., the following ones, 4, 3, 2 cm., and the bottom one, 1 cm. This arrangement will render good service, especially in the "intensive style" of working the chambers.

Littmann (Ger. P. 271077; Fr. P. 462668; Austr. P.

60969) builds vitriol-chambers of the form sketched in Fig. 31. The main chamber H and the intermediate chamber M are made successively lower, in order to counteract, by the diminution of the section, any lowering of the activity of the gases through diminution in concentration; also in order to promote the reaction by shocks of the gases (surface condensation) not merely against the back wall, but all along the length of the chambers. In the main chamber, H, the surface and the cooling may be increased by the tubes *r*. In the intermediate

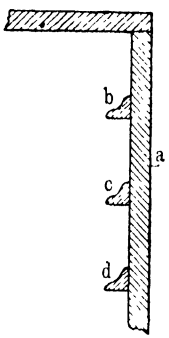


Fig. 30.

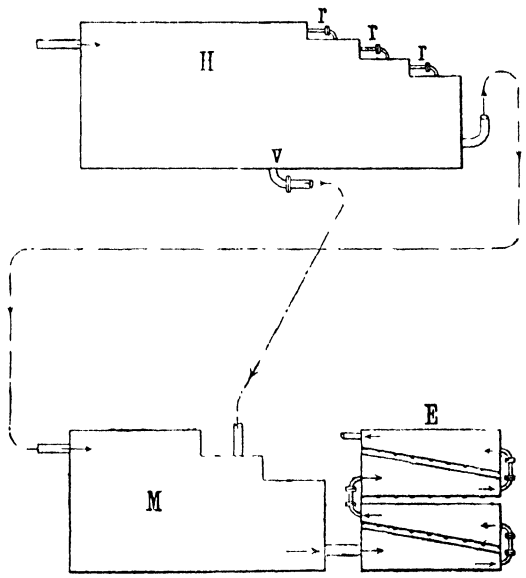


Fig. 31.

chamber, M, the diminution of the height may begin in the fore part, in order to compensate for the progressive decrease of the reaction. The last chamber, E, is divided by diagonal partitions into several intercommunicating compartments, each of which diminishes continually in section from the entrance to the exit of the gases. The gases, according to this principle, enter at a higher front wall, and go out at a lower back wall. This arrangement has the advantage over the usual end chambers of making the gases travel a long way in a small space, which greatly promotes the complete working up of the dilute SO_2 contained in the end-gases. Under abnormal

circumstances, *e.g.* at extreme temperatures of the outer air, or during temporarily intensive or restricted work, the process can be regulated at will by a suitable setting of the slides in the connecting tubes *r r*, the number of which is arranged according to the width of the chamber. For a further regulation of the work, a by-pass *v* is provided which is attached to the bottom of the main chamber, taking the sulphurous gas away from here and introducing it at will into the top of the intermediate chamber, or into the end chamber, or even into the Gay-Lussac tower. The principal object of this by-pass is the avoidance of the injurious consequences of temporary excessive separations in the chambers, by producing in the main chamber a good mixture of the gases through drawing them downwards, taking away the inactive SO_2 gases from the bottom and introducing them into the upper regions of the intermediate chamber, which may on their part be inactive on account of an excess of oxygen. Since such weak gases are not absorbed to any great extent in the Gay-Lussac towers, and also act corrosively, this by-pass causes, in addition to a uniform utilisation of the whole system, a smaller consumption of nitre and less action on the apparatus. The periodical regulation of the by-pass, apart from slide-valves, is also attained by interposing a tower fed with cold chamber acid; the upward tendency of the gases, and therefore also their quantity, can be regulated by the quantity of this acid. The tower is lined with lead, and contains an acid-proof packing of bricks, formed into the same number of shafts as that of the chambers to be charged. The by-pass gas enters at the bottom and divides itself among these perpendicular shafts, in order to leave them at the top end to supply all the back chambers, in case of need, with SO_2 gas.

Petersen (Ger. P. 295044) describes a system of constructing chambers. The framework supporting the wall is constructed of horizontal and vertical bars—for example, of round iron, gaspipe, or the like. Connecting bands partly or completely encircle the horizontal bars, and have their ends held firmly against the vertical bars by clamping devices.

The lead straps attached to the wall for the purpose of supporting it on the framework are hook- or ring-shaped, and encircle the horizontal bars of the framework. The lead wall

may consist of alternate broad and narrow strips, of which only the latter are provided with horizontal rows of straps for fixing to the framework, the broad strips hanging free.

Krantz (Ger. P. 283065) forms the bottom of the vitriol chambers in steps, each of which has an outlet for the acid. The inner margins of the steps project over their bottoms in such a way that upon these a layer of acid not exceeding 2 in. is formed; this prevents damage to the bottoms from acid drops falling down, and causes a good cooling of the gases. The superior cooling obtained by increasing the surface of chambers causes also better condensation of the acid fog before entering the Gay-Lussac tower. Each step has its own outlet for the acid, so that this can be run off at various concentrations, between 50° and 60° Bé., and only part of the acid need be more highly concentrated in the Glover tower. This construction may also be arranged for existing chambers.

F. A. Neumann (Ger. P. appl. M14024 and 14025) suspends the chamber-sides by means of horizontal lead straps from horizontal iron rods fastened to perpendicular rods which are carried by the stays arranged outside and between the chambers, but quite independent of the roof frame (this is an essential point). The perpendicular rods may be connected by transverse rods. This construction makes the chamber-top more accessible than is the case with the usual way of constructing the frame, and there are fewer places where iron is in contact with lead and liable to corrosion.

Horizontally arranged straps for suspending the side sheets of lead-chambers, in preference to perpendicular straps, are recommended by Awe.[1]

Buildings for containing Acid-chambers. — In England, where the winters are not severe, lead-chambers were until recently very rarely placed in a roofed shed, but were built so that the rain-water could run off as described above. The space between each two chambers must be covered by a light roof, and the whole set surrounded by a wooden screen, because a gale might tear the lead off the frames, or even throw down a chamber. In windy places the screens are always erected first, as soon as the foundations and the frame are finished, but before the lead has been fastened to the latter, because

[1] *Z. angew. Chem.*, 1912, p. 2523.

during the building the incomplete chamber is even more exposed to the risk of being thrown down by a gale than after completion. Thus the chamber-tops are exposed to the heat of the sun in summer and to the snow in winter. In less windy places even the chamber-sides are sometimes left without protection against the weather, but never so in well-arranged works. (In November 1911, the vitriol-chambers of the Great Lever Chemical Works at Bolton were utterly wrecked by a heavy gale, although protected on one side by a wind-screen.) In the south of France, the chamber-tops are always protected against the sun and the rain by a roof, but the sides are generally exposed, which, on account of the heat of the sun there, is certainly inadvisable. In France, in Belgium, and in other countries the chambers are always completely enclosed in buildings, usually of a very light construction, and it must be said that this is decidedly preferable in any climate.

Niedenführ recommends placing the chambers on brick pillars, and filling up the spaces between these on the outside with a light wall. The chamber-sides are surrounded by a wooden shed and a light roof, roofing-felt being employed as a cover for this.[1]

Fig. 32 illustrates a type of building supplied by J. F. Carmichael & Co., Ltd., of Liverpool, the whole structure being very substantial. They claim the following advantages for these buildings and for their method of chamber erection :—

Danger by fire eliminated and lower fire-insurance premium in consequence, as compared with ordinary timber framework. Great reduction in weight, requiring smaller foundations, as compared with timber structures. Increase in constructional rigidity and solidity, as compared with timber framework, so that it is possible to build much higher chambers ; therefore greater suitability for working with sprays, providing a considerable economy as compared with the use of steam in the chambers. Consequently the manufacturing cost of acid is reduced to a minimum. Higher chambers mean less ground space occupied.

Chambers all covered in with any kind of roofing : slate, metal, wood, or fireproof material. Chambers all boarded in

[1] See Simon-Carves system, *supra*, p. 24 *et seq.*

with wood or metal or cement slabs or brick filling between steel framework.

Greater accessibility for renewal or repairs as compared with the old system of timber framework. All steel parts are standardised and easily replaceable, being bolted together, not riveted. The lead-work is easily reached at any point, because the steel framework is much more open than timber structure. The steel-work is so designed that every part is readily accessible for painting with bitumen or acid-resisting paint.

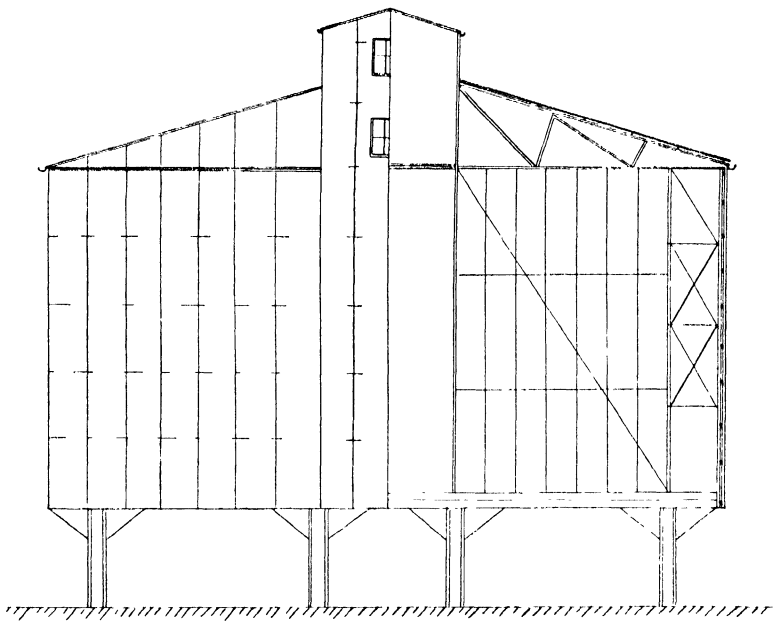


FIG. 32.

Steel framework provides for 25 per cent. better condensation than timber structure, and thus ensures a proportionate increase in output of acid per unit chamber space, causing a reduction in capital outlay on plant.

Steel framework avoids all nails for fastening lead to wood. It also avoids horizontal straps. The differential expansion coefficients as between lead and steel and lead and wood ensure a longer life for the lead and less wear-and-tear.

All lead-burning is done on the outside, except the chamber-floors. This arrangement gives security against leakage.

Ordinary repairs are thus avoided, and the lead-burning can be guaranteed to outlive the chamber-lead.

Steel framework chambers can be dismantled and re-erected without much loss of material, and they can be erected much more quickly than timber-structure chambers; thus the erection costs are reduced.

Renewal of the Chambers.—The greatest wear-and-tear is experienced in the first chamber, especially at the front end, and, as some assert, even more so at the back end and the immediately adjoining parts of the sides. Hence the first (leading) chamber is often made of stronger lead than the others. It is obvious that any angular parts of a chamber wear out more quickly than the round or straight portions; the upright corners are therefore always broken or rounded off. This is not easily managed with the horizontal top corner. Hence at some works they make the lead stronger there. The plan of making the chamber-roof partly slanting or semi-cylindrical may do some good in this respect as well, as this avoids a sharp corner. The "curtain"—that is, the part dipping in the acid—which is alternately subjected to the action of acid and air, is also liable to quicker wear. There is general agreement on the point that any part of a chamber which gets hotter than the remainder will wear out much more quickly, and this should be guarded against in the construction of the chamber-frame (*supra*, pp. 14, 15, 16, and 17).

An important point, which should be strongly emphasised, is the fact that the lead should be clear of the iron- or wood-work at all possible points, both because it is thus longer preserved by the cooling action of the air, and because it is accessible to the plumber. This condition can, of course, be realised only for the sides and top, not for the bottom. Fortunately, the latter suffers least, being protected by the acid itself and by a layer of sulphate of lead. If, however, a leak does occur here, it is very awkward to repair. Sometimes this can be done by measuring its distance from the sides, cutting a hole on the chamber-top and dropping down a bucketful of plaster of Paris or, preferably, of a mixture of fresh and burnt pyrites-dust, which quickly hardens into a cake and may stop the leak for years. A quantity of lead-ashes similarly precipitated from the top has been successfully used as a temporary

measure. If this does not succeed, there is nothing left but to stop and empty the chamber and make the necessary repair.

A chamber will last very much longer if the frame is substantially made and the straps are well burnt on so that they will not be readily torn off. If a strap should be torn off, the mischief must be repaired at once: nowhere does the saying come more true that "a stitch in time saves nine." If the repair is put off too long, the chamber-lead, pulled by its own weight, wrinkles irregularly, and the chamber becomes unfit for work much sooner than need be. Especially those parts of the frame which are most exposed to the action of the acid must be carefully looked after, and, in case of need, repaired at once, before the lead sides dependent upon them have lost their support and have collapsed. This is most necessary at the junctions of connecting-pipes, at the places where the acid is siphoned off, etc. The wind must also be kept off, and any loose pieces in the bratticing round and between the chambers promptly put right; a gale of wind may tear off the straps of a whole chamber-side at once, or force the frame to one side. The gangway round the chambers ought to be wide enough (say 4 ft.) to admit of easy control and repair.

It used to be considered that with 6-lb. lead, in normal circumstances, a chamber would generally last from eight to ten years, but would require many repairs during the later years. But since the art of building, and more particularly of *managing*, vitriol-chambers has become better understood, they have been made to continue much longer in use. On the Continent, where they are not (or formerly were not) so much strained as is frequently the case in England, vitriol-chambers generally last twenty or even thirty years; this is found to be the case at some works in England also, where the chambers are built with regard more to durability than to economy in first cost.

There is no doubt whatever that, other things being equal, a chamber lasts longer in proportion as it is less heated; the effect is due not so much to the heat itself, as to the intensity of the chemical reactions going on within the chambers, which produce the heat; and, moreover, the increase of the action of most chemicals by the elevation of temperature brings about the same result.

In the case of chambers without a roof, the top generally wears out first; after this the parts dipping into the bottom-acid and the ends; the bottom remains good up to the last, unless nitric acid gets to it, which most easily happens in the last chamber, if its strength is allowed to run down too low.

When a chamber begins to require a great amount of repairing and patching, and when the escape of the gas from the too numerous chinks and rents can no longer be kept down, it is very bad economy not to pull it down at once, for the yield of acid must fall off very much. In this case, a temporary connection is made between the two pieces of apparatus on either side of it, the acid contained in the chamber is worked down as long as it will run, a hole is cut into its side, and, when it is free from gas, men provided with india-rubber boots are sent in to shovel up into a heap the *mud* lying at the bottom, from which a good deal of acid is still obtained by draining. The mud must now be removed. If the space underneath is free, a receptacle is formed by low banks of clay or burnt cinders, a hole is cut in the chamber-bottom, and the mud pushed down. If this is not possible, it will have to be removed in a much more troublesome manner, by thickening it with sawdust. In either case, it is dried in a reverberatory furnace, sometimes with the addition of a little lime in order to prevent the escape of acid vapours. Notwithstanding this, the operation usually causes a very disagreeable stench, probably owing to arsenic, selenium, etc. The dried mud, principally consisting of lead sulphate, is either smelted for lead in a small cupola heated by coke, or simply sold.

After taking out the lead-mud, the chamber-lead is detached from the frame and melted in an iron pan. The dross is scummed off, and the lead cast in the usual moulds. Including the pig-lead, the dross, and the lead sulphate, usually nine-tenths or upwards of the original weight of the chamber is recovered. The remainder has disappeared in one form or another with the acid made.

If the frame has been substantially made, it stands a second, sometimes a third lead-chamber, with a few repairs, putting in odd beams, etc. Of course, in case of any doubt, it would be extremely bad economy to run the risk of having to stop

a chamber because its frame would not hold out as long as the lead.

Shape of Lead Chambers.—The ordinary shape of the chambers is usually that of a long box of square or approximately square transverse section. At some places, in order to save lead, the chambers have been made up to 60 ft. wide, but this is not to be recommended on any account. It causes difficulties in constructing the wood frame, and, what is more serious, the yield of acid in such wide chambers is not so good as in those of ordinary shape, say between 20 and 30 ft. wide. This is easily understood, as in such very large sections the gases do not get properly mixed, and there are too few surfaces offered for contact and cooling (*cf.* Chapter III).

The usual width of vitriol-chambers is rarely below 20 or above 30 ft. Their length (always speaking of the principal chambers) is rarely below 50 ft., but may attain 200 ft. or over.

Combination of Chambers to form Sets.

Sometimes the whole working-space is contained in one chamber. Scheurer-Kestner[1] mentions a single chamber of 142,000 cub. ft. capacity, and quotes the experience of different works, according to which it is quite unnecessary to divide the set into several chambers. More frequently, however, several chambers are combined to form a set which, to begin with, affords this advantage—that for repairs it is not necessary to stop the whole set.

A great diversity of opinion exists as to how the single chambers are to be combined to form sets. Among the hundreds of vitriol-works very few will be exactly alike in this respect, and frequently even in the same works different combinations are found. It is, however, almost immaterial in which way the chambers are combined, if they are, in the first instance, properly built (that is, neither too high nor too wide); and if, secondly, they possess a certain cubic capacity for the quantity of sulphur or pyrites to be consumed. Within these limits, those combinations are best which require least lead, and which are laid out so as to afford the greatest facility for supervision. Of course, there is also an extreme limit to the

[1] Wurtz, *Dict.*, 3, 147.

capacity of the whole set; but opinions differ upon this point also. At some works a set consists of nine or eleven chambers of 35,000 cub. ft. each; at others, equally large, it is limited to three chambers of 42,500 cub. ft. each, etc.

In France it is usual to combine three chambers in a set (in exceptional cases only, four or five). The total capacity of a set hardly ever exceeds 210,000 cub. ft.

According to *Monit. Scient.*, 1900, p. 563, Benker has for a number of years built chambers (in France) on the following plan:—Besides the Glover tower, he employs a dry filtering-chamber, in order to retain flue-dust and arsenic. His chambers are three in number, of a total capacity of only 70,000 to 105,000 cub. ft.; then comes a small intermediate chamber, followed by two Gay-Lussac towers. The draught is produced by a fan. The chambers are fed with water spray in lieu of steam, and he always injects some SO_2 (burner-gas) into the last chamber (Ger. P. 88368 and 91260). (*Cf.* Wedge, p. 200.)

Size of the Chambers.—This varies very much. Apart from the "tambours" of the French system, the ordinary chambers are made with as little as 10,000 and as much as 140,000 cub. ft. capacity. Chambers of only 10,000 cub. ft. or thereabouts are no longer built as main chambers; the usual capacity of these may now be taken as ranging from 25,000 to 60,000 cub. ft., more frequently nearer the upper than the lower limit. Smaller chambers cost much more, comparatively, than large ones, and it is doubtful whether they afford any corresponding advantages.

The different chambers of a set are either placed on the same level, or, more suitably, each following chamber is placed 1 or 2 or, better, 3 in. higher than the preceding one, so that the acid of the back chambers can be run more easily into the working-chamber. In the first chamber, the acid is strongest and most free from nitre, and it is therefore preferable to draw off any acid from this, whether it be for sale, for use, or for concentration. The acid drawn off is replaced, partly by that newly formed in the same chamber, partly by the weaker acid run over from the other chamber. If there is only one long chamber, the acid is always found strongest near the entrance of the gas.

In England and on the Continent there are now several

installations consisting of three chambers arranged according to Fig. 33, the first chamber being about 80 ft. long and the other two together the same length, less the width of the gangway.

Some manufacturers reject all preliminary chambers (tambours), because the chamber-process is carried on best if a large space is afforded at once for the mutual reaction of the gases. Thus in a large French works two-thirds of the whole chamber-space is occupied by the first chamber, two-ninths by the second, and one-ninth by the third.

The waste of lead in small chambers is more easily understood by a definite example:—A chamber of 100 × 20 × 20 ft.

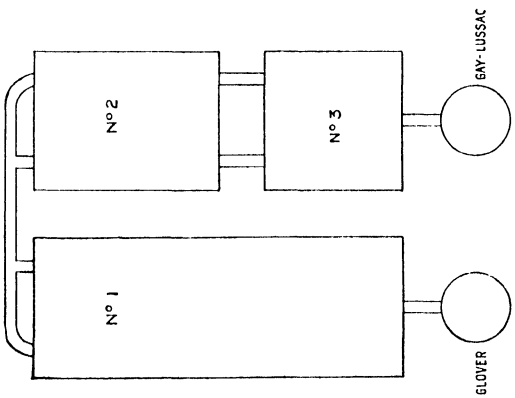


FIG. 33.

has a cubical capacity of 40,000 cub. ft. and a surface of 8800 sq. ft. A tambour of 16 × 10 × 10 ft. has a capacity of 1600 cub. ft. and a surface of 840 sq. ft. Its contents are therefore $\frac{1}{25}$ but its surface almost $\frac{1}{10}$ of that of the large chamber; consequently its surface is nearly $2\frac{1}{2}$ times as large, in comparison with its capacity, as that of the large chamber.

Whilst, of course, there is no doubt that a given cubic space of chamber-room is more cheaply obtained with a few large than with a greater number of small chambers, it is, on the other hand, very easy to overstep the mark in this direction. As seen above, in the case of chambers of an excessive section, the gases do not get properly mixed; and the same principle applies even to the division of the chamber-space in the direction of its length, since every time the gas has to be com-

pressed into a comparatively narrow connection-tube in order to pass from one chamber to another, this must bring about a good mixture, superior to that produced in the same length of undivided chamber-space. For this reason it seems expedient to subdivide the chamber-space by multiplying the number of chambers; and another strong reason for this subdivision, as will be shown later, is that the cooling down of the contents of the chamber, essential for the reaction between them, is promoted by their contact with the comparatively cool end-walls of the chambers.

In England it is taken as a practical rule that for every cubic foot of chamber-space there should be about 0·2 foot of total surface (top, bottom, sides, and ends). A chamber 20 × 25 × 100 ft. would contain 50,000 cub. ft. and have a total surface of 10,000 sq. ft., which is exactly the above-stated proportion. Sets of chambers in England are rarely made larger than 200,000 cub. ft.; if more capacity is required, the whole is broken up into two or more sets.

When speaking here, and elsewhere, of "chamber-gases," it is understood that they comprise not merely the *vapours* of water, nitrous anhydride, etc., but also the *misty* particles of liquid sulphuric acid, nitrosulphuric acid, etc., floating about in the atmosphere of the chambers.

Connections.—In the usual case, where several chambers are combined to form the acid-making apparatus, the question arises how the single chambers of the set are to be connected. One thing is certain: the *connections* must be placed at the small ends, so that the gas shall travel through the length of the chambers, thus leaving no dead corners. But the next question is, at what part of the section the connecting-tubes are to leave or enter the chambers. There is general consent as to this point, that the gas should enter the first chamber near its top. There is, however, great diversity of opinion regarding the other connections. Some take the gas away at one end near the bottom and introduce it into the next chamber near the top. Others maintain just as strongly that this is wrong, and that, on the contrary, the gas-pipe ought to leave each chamber near the top and enter the next chamber near the bottom. Others, again, contend that it matters very little where the gas enters and leaves, and that it is therefore

the simplest plan to make straight connecting-tubes about midway in the height of the chamber. This last view seems to be borne out by the practice of several men of very large experience, and it agrees very well with the investigations of Lunge and Naef (*vide infra*), who found that the composition of the chamber-gases in any given cross-section of the chambers does not differ very materially between top and bottom, so that it must be immaterial where the connecting-tubes are placed. (See *infra*.)

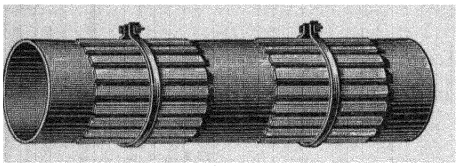


FIG. 34.

The connections may be round pipes or angular flues (tunnels). The former are preferable, because they can be made without a frame, and because they stand better. They must, however, be made of strong lead, say 9 to 12 lb. per sq. ft., and bound here and there with iron hoops, between which and the lead, wooden staves are placed in order to keep the pipes in shape; if the weight of the lead amounts to 15 lb. per sq. ft., no staves are needed. Figs. 34 and 35 will make this clearer.

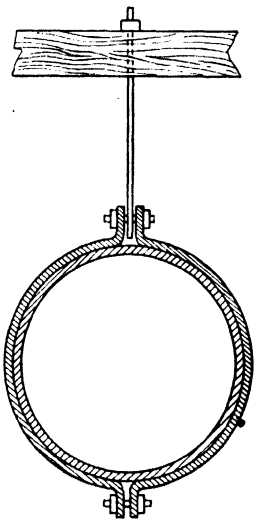


FIG. 35.

The iron hoops serve also for suspending the pipes from beams, etc. The *width* of the pipe introducing the gas into the first chamber, whether it comes from the Glover tower or from the burners, must be adapted to the quantity of gas conveyed. For a combustion of 7 tons pyrites daily, a pipe of 2 ft. diameter suffices; for 10 tons, one of $2\frac{1}{2}$ ft.; for 15 tons, one of 3 ft. diameter will do; more than 20 tons are rarely consumed for a single set in twenty-four hours. Since the volume of the gas decreases in its onward journey, the connecting-pipes between the single

chambers may be successively a little smaller; it should be remembered, though, that whilst no harm is done if the pipes are too large, very much may be done if they are too small.

Hegeler and Heinz (U.S. Ps. 728914, 752377; B. P. 254 of 1904) arrange the flues to enter the side of the chamber near the front end, and to pass out of the side at the rear end, at different levels, and transversely to the length of the system. The gases thus enter and pass out of the chambers in opposite directions, at different levels, and transversely to their general course. Their U.S. P. 765834 describes a main flue provided with a filled section and a free open section, with a fan in the free section, and a secondary flue communicating with the main flue before and after the filled section, also provided with a fan.

According to the B. P. 20012 of 1904, of G. E. and A. R. Davis, the chambers are connected by tubes of 2 or 3 in. diameter, of which forty (more or less) are employed, so as to afford the necessary space for the gases to travel through. They are stated to have a very efficient cooling action, being exposed to the atmosphere (this is identical with the Griesheim plan, described in Lunge's edition of 1903, vol. i. p. 465).

In the *41st Alkali Report*, pp. 91 and 92, it is stated that several firms had changed the connections of the chambers so that the inlet is near the bottom, and this has been found very satisfactory. The steam is introduced above the inlet and below the outlet.

Porter[1] strongly recommends placing the entrance-pipe for the burner-gas at one end of the chamber near the bottom; not, as is found in most places, in the centre or near the top. His opinion is founded on experiments made with a glass model on a scale of $\frac{1}{4}$ in. to 1 ft. The exit-pipe should be about half way up the middle at the other end.

Höfling (Ger. P. 202631) places spiral-shaped plates in the entrance- and connecting-pipes of the chambers in order to give a rotating movement to the gases. In case of several entrance-pipes (which may be arranged at an angle to one another) the spirals are made alternately right- and left-handed so as to produce a more intimate mixture of the gases.

Thiele (U.S. P. 1267012 of 1918) also connects the Glover

[1] *Chem. Trade J.*, 1909, **44**, 79.

tower to the first chamber by a number of pipes, but these enter tangentially and are of different lengths and sectional areas, the smallest pipe having the greatest length and the largest pipe having the shortest length. A number of outlet-conduits are arranged concentrically in the bottom of the chamber on a diameter approximately half the diameter of the chamber.

Cubical Contents of Chambers.—The total cubical contents of a set of chambers must bear a certain proportion to the quantity of acid to be produced, several special circumstances modifying that proportion. Thus it is certain that for pyrites, more chamber-space is needed than for sulphur; as seen (p. 457 of Vol. I), the relative proportion may be stated as 1·314 : 1. Properly speaking, the connecting-pipes (if they are of great length) and the Glover and Gay-Lussac towers should also be included in the calculation, and that to a larger extent than corresponds to their cubical contents.

The consumption of nitre also influences the chamber-space; within certain limits, a larger consumption of nitre may compensate for a smaller space.

The widely divergent views on this point may be explained partly from this, but not entirely, for some manufacturers obtain about the same yield as their neighbours possessing half as much more chamber-space, although both the pyrites and the general construction of the plant and their consumption of nitre are practically the same. In the following remarks all measures are reduced to cubic feet of chamber-space required for burning 1 lb. of sulphur daily, taking, in the case of pyrites, the sulphur charged into the burners.

Particulars are given below of the chamber-space found in various works in England which the writer has inspected; the source of sulphur, capacity of the Gay-Lussac towers, with the packing used, being also added.

No.	Material burned.	Tons burned per week.	Per cent. S.	Capacity Gay-Lussac on chamber-space, per cent.	Packing used in Gay-Lussac.	Cub. ft. per lb. S. per 24 hours.
1	Pyrites	42	43	5·0	Coke	16
2	,,	...	50	3·2	Rings	12
3	,,	117	40	1·6	Glass	12
4	,,	180	45	3·0	Coke	13
5	Spent oxide	32	52	0·9	Glass	14
6	,, ,,	60	46	2·3	Coke	16
7	,, ,,	80	50	1·5	Glass	15
8	,, ,,	126	50	5·0	Rings	10
9	Coal brasses	19	40	4·4	Coke	25

The above figures relate to ordinary workings with the usual rectangular chambers, and no attempts were made to work intensively. For plants dealing with sulphur, 30 to 50 per cent. less space could be allowed. In the case of plants erected in hot climates, it is usual to allow 12 cub. ft. per lb. of sulphur per twenty-four hours, where pyrites is the source of sulphur. Of course, the *sine quâ non* for lower chamber-spaces is ample Gay-Lussac capacity, and, in those plants which are said to work at 2 or 4 cub. ft., this is provided. (See *infra.*)

According to H. J. Bailey,[1] the chamber-space throughout Great Britain in 1917 was 16·5 cub. ft. per lb. of sulphur per 24 hours.

Intensive or High-pressure Style of Working.

In recent times, a new style of working has been introduced, first in several French works, called "*production intense*," say "forced" or "high-pressure" or "intensive" work. It consists in supplying the chambers with a greatly increased stock of nitre, the nitre being recovered by means of largely increased Gay-Lussac and Glover towers; in this way the production may be increased to almost twice the usual amount. Frequent mention will be made in later parts of this book of this "intensive" style, which was formerly confined to French factories, but is now practised elsewhere as well.

The ordinary production can also be increased by the use of artificial draught (fans), by "tangential chambers" (*cf.* p. 60), by reaction towers, and by other means described in their places.

[1] *J. S. Chem. Ind.*, 1921, p. 248R.

Petersen[1] greatly recommends this high-pressure style. He does not, from his experience, believe that the chambers suffer under it more than in the ordinary way, but much more nitre must be introduced.

He also gives numerous details with regard to the working of his regulator in conjunction with duplicate Glover and Gay-Lussac towers. Fig. 36 shows the arrangement, the arrows showing the circulation of the various acids.

The regulator "R" is placed before the first Gay-Lussac, and is circulated with acid maintained at from 119° to 134° Tw., and acts in such a way that the excess of nitric oxides

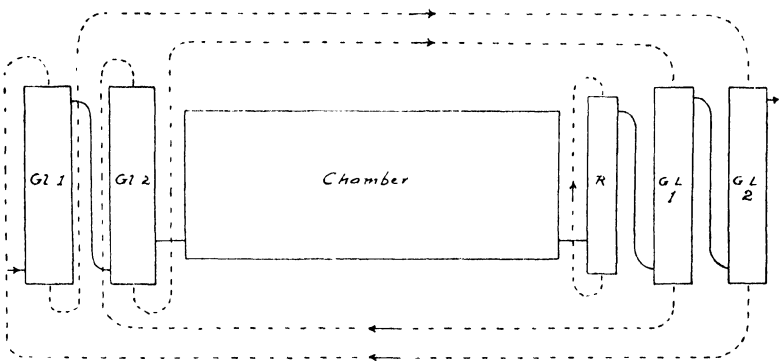


FIG. 36.

is absorbed from the chamber-gases in case the supply of sulphurous acid is reduced; when there is an excess of the latter, the "nitre" compounds are given up (U.S. P. 904147). In this way there is a better control of the process, and a more intensive working is possible.

Sulphurous acid may therefore be allowed to leave the chamber without fear of nitric acid being formed, and thus the wear and tear of the leadwork is reduced.

When working the chambers at a low capacity, the regulator is also useful, and even in intensive work there is generally a saving of 25 per cent. of nitre and a 20 per cent. increase in the output of a plant after the introduction of his apparatus.

W. Kauffmann (Ger. P. 340030 of 1919) arranges circular, polygonal, oval, or elliptical chambers so that the gases under

[1] *Z. angew. Chem.*, 1907, pp. 1101-1105.

100 mm. water pressure or more should enter by one or several connections at the same height or at different heights above the bottom. These connections are arranged so that the gases take a spiral course through the chamber.

The Benker-Millberg system for the intensive production of acid is described in *Chem. Eng.*, vol. xi. p. 118-121.

This system is characterised by the use of two leading-chambers between which the gases are divided immediately after the outlet from the Glover tower (Fig. 37).

In comparing this new system with an ordinary three-chamber one, Benker states that his two leading-chambers are of a total capacity equal to the first chamber of the ordinary style. Each of the twin chambers, therefore, only receives

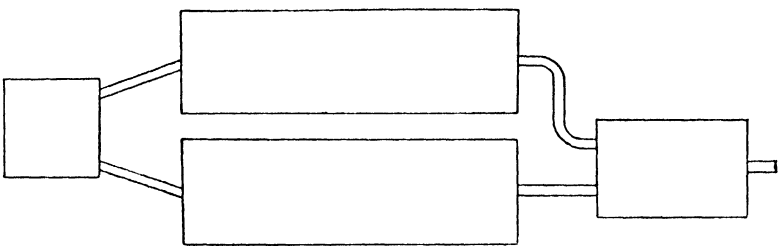


FIG. 37.

half the volume of the burner-gases. From the end of these chambers he then allows the gases to mix and enter another chamber.

It is easy to understand that in two acid sets of the same chamber-space and the same production, the lead in the Benker system is exposed to a temperature much lower than that in the single first chamber of the other set, and that this lower temperature means an increase of production.

If, on the other hand, a manufacturer does not desire, for special reasons, to increase his production beyond the ordinary limits of intensive production, that is to say, 9·5 to 8·8 cub. ft. of chamber-space per lb. of sulphur burnt, it is just as advantageous to adopt the Benker-Millberg system, because, owing to the advantage of working at a low temperature, he avoids much of the wear of the lead, compared with a single first chamber for the same production.

The division of the gases between the two first leading-

chambers is effected automatically without dampers. When, for instance, the production of acid in one of the chambers diminishes owing to shortage of gases, a fall of temperature in this chamber is necessarily produced. Through this fall of temperature the chamber begins to draw more, and thus an automatic equilibrium is established. This equilibrium is so perfect that the variations or differences of temperature or production between the two chambers are insignificant.

It is to be observed that, in employing the twin system, the production in the first part of the set exceeds that in any system previously used, and consequently the last chambers of the system produce less acid.

The reaction of the gases in the second chamber is accelerated by the more complete mixing in the two connecting-pipes, compared with that in the single pipe of the older systems.

J. Thede[1] describes the results of intensive working on a plant consisting of a four-chamber system, in which the second and third chambers were 21 ft. high, and the first and fourth respectively 17 ft. and 16¾ ft. high. The first chamber was provided with an extension 23 ft. in height for the introduction of the gases, and the lead mantle of the Glover tower was attached directly to the brickwork, the air-cooling being so efficient that little repair work was necessary. The burner-gases containing 7 per cent. of SO_2 were forced by a wrought-iron fan into the Glover tower at about 500°, whilst there was a second fan of hard lead between the first and central Gay-Lussac towers.

As a rule, the amount of circulation acid is equal to two to four times the amount of acid produced, but in this plant the amount reached 1000 per cent. for the Glover tower and 500 per cent. for each of the Gay-Lussacs.

Gaillard (Fr. P. 528080, Ger. P. 346121)[2] seeks to prevent undue wear and tear of the chamber-plant by the use of a turbine just underneath the centre of the top of the chamber, which latter is an inverted truncated cone. The turbine is fed with cold, somewhat dilute acid, which is projected outwards against the upper part of the sides. Some of it trickles down

[1] *Z. angew. Chem.*, 1918, **31**, 2-3, 7-8; *Absts. Soc. Chem. Ind.*, 1918, p. 464.

[2] *Abst. Soc. Chem. Ind.*, 1922, p. 291.

the sides, and the remainder falls as a mist of dilute acid. The chamber-walls are thus cooled, and also protected against the action of nitrosyl sulphate. Connecting-pipes are similarly protected by sprays, and the use of cold-water sprays in the chamber is dispensed with. A plant constructed on this principle has given an output of 15 kg. of 53B (sp. gr. 1·58) per cub. m. of chamber-space = 4·7 cub. ft. per lb. sulphur per 24 hours.

P. Parrish[1] describes the Moritz type of cylindrical tower-chambers, of which ten were used in series, their height being 32 ft. 6 in. and diameter 14 ft. 9 in.

Pyrites was the source of sulphur, and the mean strength of the acid produced in the whole series was 1·58 sp. gr. Water-sprays were used, and the production of acid was equivalent to 8·3 kilos of acid per cub. m., representing 5·9 cub. ft. of chamber-space per lb. of sulphur per 24 hours.

C. H. MacDowell (U.S. P. 1402941, 1922) sprays a large amount of dilute acid into the chambers, and it is stated that it is possible to work with 6½ cub. ft. chamber-space per lb. of sulphur per 24 hours.

The Unione Italiana fra Consumatori e Fabricani di Concimi e Prodotti Chemici, and Antonin Sonneck (B. P. No. 164627, 1921), describe a series of vertical chambers of great height in proportion to their horizontal cross-section, with communications only at their lower portion, the inlets being placed at a higher level than the outlets in order to avoid the possibility of the gas passing directly through the chambers.

The movement of the gas is said to be upwards and towards the centre of the column; then they descend towards the surface of the walls, thus causing a double current of the gas. Water-sprays are arranged in the top of the columns.

Cost of Repairs.—An important paper on the "intensive" or "high-pressure" working of the acid-chambers has been published by Nemes.[2] He points out that very naturally every acid-maker wishes to make the fullest possible use of his plant; but whether it is really more economical to work at 18 to 9 or 6 cub. ft. per lb. sulphur per 24 hours is a question not yet finally decided. Concerning the history of

[1] *Chem. Age*, 8, 1923, p. 693.
[2] *Z. angew. Chem.*, 1911, pp. 387-392.

the "intensive" chamber-working, see the German edition of Lunge's *Sulphuric Acid and Alkali* (third English edition of 1903, vol. i. pp. 453 and 468).

Nemes declares (*ibid.*) that, contrary to the general assumption, *the intensive or high-pressure style of working the chambers leads to higher costs of producing the acid than a normal 12 cub. ft. of chamber-space per lb. sulphur per 24 hours*, owing partly to the comparatively great wear and tear and the consequent higher cost of amortisation and repairs, partly to the increased consumption of nitric acid. It has now been proved that in the high-pressure style there is greater wear and tear of the lead, for the temperature is higher and the amount of nitric acid in circulation is greater. There is also a greater quantity of sulphuric acid condensed on the lead, which washes off the protecting coat of lead-mud. The conclusion is: that for new erections the intensive style should not be chosen, and the adoption of this style can be advised only for special cases, such as the impossibility of enlarging a factory, or special conditions of trade, or the stoppage of another set of chambers for repairs, and so forth.

Finally, Nemes briefly compares the manufacture of sulphuric acid in chambers with the production of sulphuric acid without chambers, in towers, etc., as described in a later chapter. He considers that it is yet too early to come to a definite conclusion on this point, and several years' further experience is required before the cost of acid by these systems can be definitely calculated.

Petersen[1] very strongly opposes the statements and views of Nemes, and criticises his comparative tables on the costs of erecting and working chambers by different systems, which are calculated on quite arbitrary assumptions as to the costs of repairs and the life of the chambers. He also objects to Nemes basing his comparison of the consumption of nitric acid in the various systems on antiquated data. Nowadays factories working at 7 to 9 cub. ft. of chamber-space per lb. sulphur per 24 hours should never use more than 1 per cent. nitric acid 36° Bé., and he quotes a case where only 0·6 per cent. was used by the Falding system (*vide infra*); only 0·8 per cent. nitric acid 36° Bé. is required when working at 7

[1] *Z. angew. Chem.*, 1911, pp. 877-881.

cub. ft. per lb. sulphur per 24 hours. Petersen considers the principal advantage of the high-pressure system to be the saving of 30 to 50 per cent. capital, which allows quicker amortisation. He concludes with a comparison of Meyer's and Falding's chambers, which will be quoted when the latter are dealt with. (*Cf.* p. 58.)

Th. Meyer[1] points out that "intensive work" can be produced by various styles of apparatus, but will be always connected with a greater expenditure for nitre and repairs, and that the optimum of work will lie between the extremes.

Nemes[2] replies to various criticisms of his paper, and insists that the production-costs in the system advocated by him are no higher than in the ordinary style of work.

Hartmann[3] states that it is possible to maintain good results even when working at 6 cub. ft. chamber-space per lb. of sulphur per 24 hours, so far as the consumption of nitric acid, high-pressure air, cooling-water, and wages are concerned, but that the advantage is partly, sometimes even more than completely, counterbalanced by a considerably greater wear and tear of the chambers. Hence such intense working of the chambers has now been given up, and 10 cub. ft. of chamber-space per lb. sulphur per 24 hours may be taken as normal. The Glover towers did not wear out more quickly than ordinarily by the intensive work.

Hasenclever[4] considers it advisable to be satisfied with a production equal to about 11 cub. ft. of chamber-space per lb. of sulphur burnt in 24 hours. When the production is increased above this, the cost of chamber repairs rises considerably.

In conclusion of this summary of the advantages and drawbacks of the "intensive" style of working, the impression of the writer is, that that style is more and more extending, and the most advanced manufacturers of sulphuric acid seem decidedly on the side of the "intensive" work.

In the *57th Alkali Report* (1920), p. 15, the following occurs: "Where new installations are contemplated, factors now come into play which were either unknown years ago or

[1] *Z. angew. Chem.*, 1911, p. 1520.
[2] *Ibid.*, p. 1564.
[3] *Ibid.*, p. 2302.
[4] *J. Soc. Chem. Ind.*, 1911, p. 1292.

did not possess the same importance that they do to-day. Intensive working has much to be said for it, and in these days, ground-space and materials of construction are points carrying much greater weight than they used to do."

Other Proposals for Diminishing the Chamber-space.

The considerable ground-space taken up by the ordinary vitriol-chambers, and the very large capital required for these immense leaden structures, also the expense of the correspondingly vast buildings containing them, has led to a great many proposals for restricting the chamber-space, or for doing away with lead-chambers entirely and substituting cheaper apparatus for them.

Most proposals for manufacturing sulphuric acid in a diminished space start with the assumption that, in the ordinary vast chambers, the gases are not sufficiently well mixed. Some of them also assume that there is not enough "condensing" surface for the sulphuric acid, and that this should be artificially increased. The assumption that the sulphuric acid required to be condensed from a vapour to a liquid, similar to the condensation in distilling alcohol, is, of course, wrong, inasmuch as the sulphuric acid is liquid as soon as formed, and does not exist at all in the chambers in the state of vapour. It will be shown further on, that, for other reasons, it is certainly true that a large amount of *surface* for the chamber-gases to impinge on is a most important factor in the chamber-process, and that, moreover, a certain amount of *cooling* is also of great importance. Partitions, however, within the chambers, if made of lead, are most quickly corroded; if made of glass, they soon collapse.

Ward (B. P. 1006 of 1861) proposes a special mixing-chamber, followed by a second lead-chamber, or flue, 200 ft. long by 3 ft. high and 3 ft. wide, almost filled up with sheets of glass for a length of 25 ft. The sheets lie in a horizontal position, and are kept a little apart by strips of glass, to permit the passage of the gases. Ward believed that nitrous vitriol would condense upon these sheets and present a large surface to the sulphuric acid. The horizontal arrangement is unfavourable to a systematic action of the gaseous and liquid

agents, for which streams in opposite directions (up and down) are preferable, as will be seen below; and the total lack of a cooling arrangement would make the reaction on the solid surfaces incomplete. This, however, will be referred to later on.

Mactear[1] carried out some experiments to show the importance of surface condensation. A tray, 1 sq. ft. area, placed in a vitriol-chamber, was found to give 708 grams H_2SO_4 in twenty-four hours. By placing in the tray twelve pieces of glass, 12 in. by 6 in. each, in a vertical position, the amount of acid obtained in twenty-four hours rose to 1644 grams, or 2·3 times as much; and by placing the glass slips horizontally, the same distance apart as before, the amount of acid rose to 3226 grams, or 4·5 times more than without the glass. Other experiments made with "surface condensers" within the chambers showed that in the case of flat vertically placed sheets the side facing the gaseous current condensed more acid than the opposite side, in the proportion of 100 : 78. When the same plates were placed horizontally, with their edges facing the current of the gases, the amount obtained from the double surface was 172, against 178 in the former case.

The principle of surface condensation is also employed in de Hemptinne's chamber-system, in connection with his system of concentration.

Walter and Boeing (Ger. P. 71908) employ hollow partitions made of acid-proof material, arranged across the whole width of the chambers.

Brulfer (Fr. P. 220402) also employs hollow brick partitions within the chambers; he adds dividing apparatus, made of air-cooled lead tubes, fixed behind each partition. When the gases have passed through a cooled divider, they again travel through a hollow brick divider.

A similar principle, in which, however, the idea of mixing the gases was the chief aim of the inventors, is involved in the proposal made by Gossage and many others, and frequently carried out in practice, of *filling the chambers partially or entirely with coke*, or of erecting special coke-towers at the end of the set, not as Gay-Lussac towers, but to be merely moistened by water or steam. In practice it has been found that, even as a matter of construction, this plan gave much trouble, because

[1] *J. Soc. Chem. Ind.*, 1884, p. 228.

the great weight pressing upon the outside layers of the coke makes it bulge out or even cut through the chamber-sides. But apart from this it was found that the yield of acid for a given chamber-space was *not* increased, that more nitre was consumed, and that the acid was rendered impure by the coke. Everywhere, therefore, the coke has been removed from the chambers. The cause of this failure is probably twofold: firstly, the injurious action of the coke on the nitrous gases, which would thereby be reduced with formation of carbonic acid (*cf.* Chapter II); secondly, the lack of any cooling, just as in Ward's case (p. 52).

Fromont (Ger. P. 191723, B. P. 4861 of 1907, Fr. P. 375117). In order to increase the available cooling surface of the lead-chambers, the walls are provided with undulations with, or without, radiating-plates, or with radiating-plates only; or the chambers may be provided with re-entrant parts, in which case the walls may be undulatory or provided with radiating plates as described above. The undulations are preferably arranged vertically, and to increase radiation the walls may be matted, roughened, or unpolished. In addition, the roof of the chamber may be elliptical and provided with undulations, with or without radiating plates; or the chamber support may be entirely metallic, extending the whole height of the chamber and arranged to allow for its expansion and contraction, and also so that there is sufficient space between the walls and framing to allow free circulation of the air.

Dawson (B. P. 135359) obtains a more intensive working of the chamber-process by passing the gases from the Glover tower into one end of the chamber at about one-third of its height, where they impinge upon barriers extending right across the chamber. These barriers are composed of acid-resisting brickwork. The acid which collects at the bottom of the chamber is pumped up to the top and caused to flow over the barriers by distributors.

Mechanical Gas-mixers.—That mixing the gases alone is not sufficient is proved by the small success of Richter's apparatus (Ger. P. 15252), consisting of a steam-injector on the top of the chamber, which aspirates the gases from the lower part of the chamber and reintroduces them at the top. It is true that by this apparatus probably only a small portion of the gases would

be set into circulation ; otherwise the draught would have been interfered with to an impracticable degree.

The same proposal has been made in a somewhat modified form by N. P. Pratt (B. P. 4856 of 1895). He places a fan or steam-injector in front of the chamber, and a tower, fed with weak sulphuric acid, at the end of the chamber, the gases issuing from the top of this tower being re-injected into the chamber by means of the fan. Baffling-columns may also be placed within the chamber. Modifications of this system by the same inventor are described in the U.S. Ps. 652687 to 652690, and B. P. 10757 of 1899.

Guttmann[1] also recommends placing the mixing-fans in front of the chamber—not, as some have done, at the end of it.

Rabe (Ger. P. 237561) applies the theory of Abraham, which will be explained in Chapter III, to produce a spiral movement of the gases in vitriol-chambers, either by mechanical means or by sprays of cooled sulphuric acid of lower strength than chamber-acid, the spray being produced by chamber-gases. A further patent of his (Ger. P. 240474) seeks to secure the mixing of the gases in another way. In order to prevent the hot gases, coming from the Glover tower, from flowing along the top of the chamber, partitions are provided at right angles to the direction of the gaseous current, reaching some distance downwards from the chamber-top (from which they are suspended), and, if necessary, cooled by water ; or a similar effect is produced by making the chamber-ceiling inclined from the entrance to the outlet.

Th. Meyer's "tangential chambers" also belong to this class of apparatus (*cf.* p. 60).

Burgemeister proposed both to *mix and to cool* the gases by arranging a number of lead pipes, 15 to 18 in. wide, vertically between top and bottom of the first chamber, and cooling these by air passed through. This plan is hardly practicable, as the great increase in the number of joints, especially at the bottom, will cause too many interruptions for repairs. It can, however, be more easily carried out, according to Hartmann,[2] by constructing these inner pipes or shafts in the same manner as an ordinary chamber-bottom—that is, with a hydraulic lute, formed

[1] *J. Soc. Chem. Ind.*, 1903, p. 1332.
[2] *Chem. Zeit.*, 1897, p. 877.

by turning up the chamber-bottom round the bottom of the pipes. Hartmann employed a number of these shafts, 5 × 6 ft. wide, and thereby obtained an increase in the production amounting to 20 per cent., viz., 14½ to 16 cub. ft. chamber-space per lb. sulphur burned per 24 hrs. (This is not particularly good.—W. W.)

F. Blau (Ger. P. 95083) injects a spray of cooled sulphuric acid into the first hot part of the lead-chambers in order to keep down the temperature, and a spray of hot acid into the last part of the chambers in order to accelerate the reaction here, which is otherwise slow. If the exit-gases thereby become too hot, they are cooled by a spray of cold acid before entering the Gay-Lussac tower.

Davis (B. P. 15459 of 1912) arranges transverse shafts with agitating-blades in a chamber, and divides each chamber by a partition into two compartments. The revolution of the blades causes the acid to be squirted over from one compartment into the other, and circulation is effected by an outside water-cooled channel.

Thomson-Houston Co. (B. P. 15293 of 1913) arrange a blower to secure a movement of the gases through the plant and to act by induction on the column of gases flowing from the last chamber of the system. Its speed is controlled by a device responsive to variations in the volume of gases passing out of the chamber.

Wentzki (Ger. P. 238739) employs cylindrical chambers fitted with mechanical contrivances.

J. A. Hart (Ger. P. 272984) describes an arrangement for causing a mutual action between liquids and gases or vapours, by dividing the gas into many small currents, directed tangentially to the curvature of the concave plane of conduit.

In the *Alkali Report*, No. 56 (1919), p. 19, the Chief Inspector deals with the question of circulating the gases in the chamber by a steam circulating device, and Figs. 38 and 39 illustrate the arrangement he recommends. Chance & Hunt, Ltd., fitted three of these to one of their chambers, with the result that they found excellent circulation taking place and that they were an improvement over the ordinary steam-jet. In another works in particular, very marked results were obtained by means of one injector fixed at the back end of a

chamber in which, owing to unusual conditions, the drips at

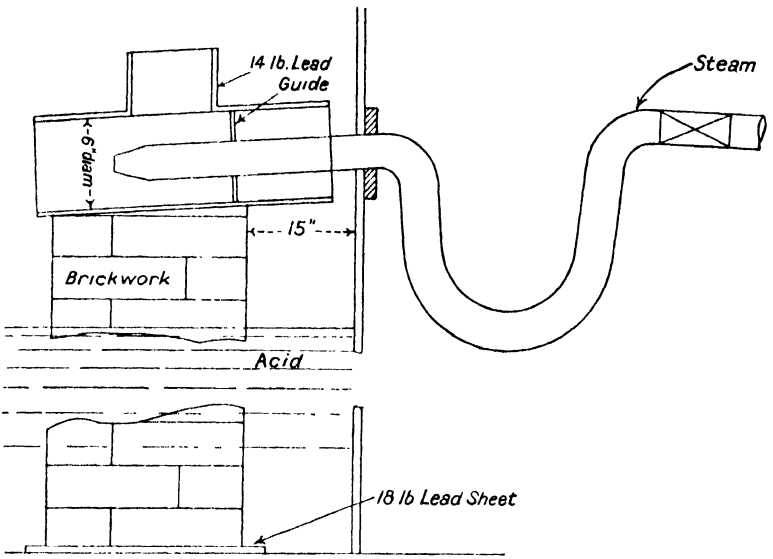


FIG. 88.

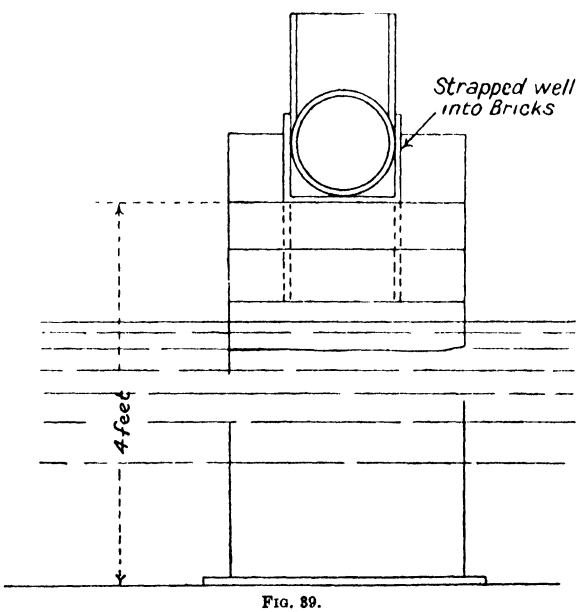


FIG. 89.

the front end showed 110° Tw., whilst those at the back end

showed 124° Tw. The result of the introduction of the circulating injector was an almost uniform drip of 118° Tw.

Special Types of Chambers.

E. and T. Delplace (B. P. 5058 of 1890) describe an *annular* chamber, in which the gaseous current is continually changing its direction, owing to the shape of the chamber. Siphon-shaped tubes placed on each side of the chamber produce a circulation and mixture of the gases. These chambers occupy less space than the usual form, and are stated to work at 1 lb. sulphur to 13·2 cub. ft. per 24 hours. The production from these chambers per cubic foot does not, therefore, exceed that of ordinary chambers.

Falding's Chamber.—A new style of chambers has been introduced by Fred J. Falding (U.S. P. 932771 of 1909; B. P. 26452 of 1909; Fr. P. 410556; Ger. P. 241509), about which he reports in *Eng. and Min. J.*, 1909, p. 441 *et seq.*, and *J. Soc. Chem. Ind.*, 1909, p. 1032. Starting from considerations as to the production of heat in the process and to the convection currents set up thereby, he employs only one chamber (together with a cooler), of much greater height than had been previously used, up to 70 ft., with a horizontal section of 50 × 50 ft., and shows a saving of about 40 per cent. of lead in high chambers of Falding's system for the same cubic capacity and irrespective of the increased efficiency of chamber-space. In his system the gases leave the chambers too moist and too hot to permit their direct admission to the Gay-Lussac towers, and they must first be dried and cooled. This, however, can be done with much greater economy than by providing additional chamber-space. The results quoted from actual work are very satisfactory. There is no SO_2 left over when the gases leave the chamber, and the consumption of nitrate is reasonably low. The saving in ground-space is about 60 per cent. The chambers are erected on a slab of reinforced concrete, covered with ¾ in. asphalt, perfectly smooth, in order to receive the bottom lead of the chamber. The framework consists of steel side-trusses with Z-bar posts, bolted to anchorage in concrete piers, and connected by angle-iron horizontal bars. These bars are connected with the walls of

the chamber by continuous horizontal lead straps, burned to the lead sides, and clamped and bolted to the angle-iron girts so that the angle-iron is in contact with the strap only and does not touch the lead sheets. The roof trusses are connected by angle-iron joists. The framework is rigid and strong, and affords easy access for repairs and painting, and at no point does it come in contact with the chamber-lead. The chamber-system consists of a cooler and a single high, tower-like chamber, into which the reacting gases are introduced at the top, and from which they are taken away at the bottom. The proportion of height to diameter is as 3 : 2. The gases go first through a Glover tower, then into the chamber, then into a small cooling-chamber (also entering at the top), and lastly into a Gay-Lussac tower. The cooling-chamber and the Gay-Lussac are cooled by running water over them. The large chamber is not cooled, but is sprayed with nitrous vitriol.

Petersen [1] compares the systems of Falding and of Th. Meyer (*tangential chambers*, p. 60) as follows:—(1) The production in Falding's chambers, for the same consumption of nitre, is greater than in Meyer's chambers. (2) The former require only about half as much ground-space as the latter. (3) The action of the gases on the chamber-lead is much less in Falding's system, where the gases descend uniformly in the chamber, than in Meyer's system, where they are as much as possible brought into contact with the chamber-walls. (4) Much less lead is required by Falding than by Meyer, as proved by the figures given above. Petersen repeats his commendation of Falding's chamber in his reply to a paper by Th. Meyer in *Z. angew. Chem.*, 1911, p. 1520, *eodem loco*, p. 1811.

Hartmann [2] considers Falding's system inferior to the tower systems on account of requiring too much power for pumping acid. Petersen [3] defends the system against that objection. Keppeler [4] asserts that it has not been practically successful.

Falding and Cathcart [5] attribute the superior action of their

[1] *Z. angew. Chem.*, 1911, p. 880.
[2] *Ibid.*, 1912, p. 381.
[3] *Ibid.*, p. 762.
[4] *Jahresber. d. chem. Techn.*, 1912, p. 381.
[5] *J. Ind. Eng. Chem.*, 1913, p. 223.

high chambers to the special conduction of heat taking place in them. The first Falding chamber was started on 1st January 1907 at Vandergrift, and was followed by the plant of the Tennessee Copper Company at Copperhill (thirty-six chambers), and many others. Experience has proved the following advantages of Falding's system over the ordinary vitriol-chambers :—(1) Saving of lead ; for a given production the weight of lead is only 141,000 lb. against 240,000 to 300,000 lb. in the ordinary horizontal vitriol-chambers, or 220,000 lb. in Th. Meyer's tangential chambers. (2) Large amount of work done ; 6 to 7 cub. ft. of chamber-space for 1 lb. of sulphur burnt. (3) Large saving of ground area and foundations. (4) Security against fire and gales. (5) Saving of wages in working.

R. Hoffmann [1] describes the Falding plant at the Tennessee Copper Company's works. It produced per annum 140,000 tons sulphuric acid, 60° Bé., from 400,000 tons poor copper ores, mostly pyrrhotite, with a little pyrites, which was smelted for matte in blast-furnaces. The Ducktown Sulphur, Copper, and Iron Company also work up the gases from the pyritic smelting in Falding chambers, obtaining 50,000 tons of acid of 60° Bé. from 150,000 tons of ore containing 14 to 19, on the average 16, per cent. sulphur.

Meyer's tangential chambers (B. P. 18376 of 1898) are built in sets of three, and are 32 ft. 10 in. diameter. The general arrangement will be gathered from Fig. 40 below. The gases from the Glover tower enter the first chamber at the top of the side wall, the entrance-pipe forming a tangent to the periphery of a chamber. The steam-nozzle is introduced at the same point, the steam being directed in the same path as the burner-gases. The outlet for the gases is a pipe in the centre of the bottom of the chamber, the stump of the pipe being sufficiently long to allow the acid to lie in the bottom of the chamber, and a cover is loosely fitted over the top to prevent the dripping of acid into the pipe. The pipe leads upwards from the bottom of the first chamber to the top of the second, which it enters in precisely the same way as into the first. From the second chamber to the third the course of the gases is the same, and from the third they go into the Gay-Lussac. The

[1] *Chem. Zeit.*, 1913, p. 1217.

pipes from the chambers have trapped over-pipes to run out any acid condensed in them.

The principle underlying the invention is that the gases are directed into a circular chamber in such a manner that they circulate round and round before finding their exit from the centre.

The effect of this is, that the gases travel a very long way, their course being somewhat in the form of a spiral or screw. A very much improved intermingling of the gases is effected, and the contents of the chamber acquire a rotary motion; the action of the chambers may be said to be analogous to stirring a soluble substance in a solvent to effect a more rapid solution than would be obtained by leaving the liquid at rest.

Later on,[1] Meyer improved his chambers by arranging in

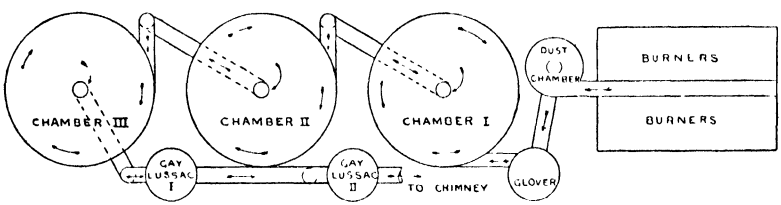


FIG. 40.

the first (and hottest) chamber a *cooling system*, consisting of forty-three lead pipes, 2 to 2½ in. wide, suspended in water-lutes from the chamber-top all round the circumference and reaching 8 to 10 ft. down into the chamber. They are closed at both ends; through their tops enter thin lead pipes, reaching nearly to the bottom of the larger pipes, for introducing the cooling-water, as shown in Fig. 41. The whole offers a cooling surface of 250 sq. ft., *i.e.* 7 per cent. of the heat-radiating surface of the chamber sides and ceiling. The water, of which 8½ tons is used per day, issues at a temperature of 67°. The heat evolved by the process of converting SO_2, O, and H_2O into H_2SO_4, as far as it goes on in that chamber, is calculated at 2½ millions metric heat-units per twenty-four hours, of which 500,000, or 20 per cent., are removed by the cooling-water. This is not shown by the chamber thermometers, as the loss of heat is made up by that generated by

[1] *Z. angew. Chem.*, 1900, p. 742.

the chemical process, but it is manifested by the increased production of sulphuric acid (according to the theories of Lunge and Sorel, *cf.* later on). The pipes last a long time, and can be immediately renewed by taking them out of the hydraulic seals. The hot water is used for feeding the steam boilers.

In *Z. angew. Chem.*, 1902, p. 151 *et seq.*, Lunge stated that the advantages to be realised by Meyer's proposals, on his own showing, are not very considerable. It is very doubtful whether for equal weights of lead his tangential chambers produce any more than even moderately well-managed ordinary chambers. This also comes out in the comparisons made by Falding (see above).

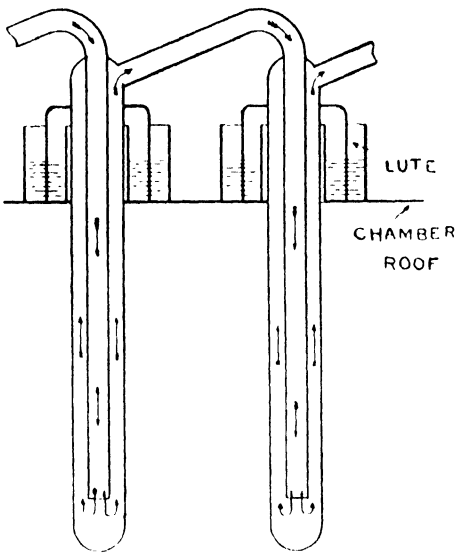


FIG. 41.

Th. Meyer (Ger. P. 186164) later patented an improvement of his "tangential chambers" by placing two or more tangential inlet-pipes in various places of the chamber-walls. Another improvement by the same inventor and described in Ger. P. 226792 is made for the purpose of dealing with the fact that a stagnation of the gases takes place round the exit-pipe at the bottom of the chamber. This is now remedied by providing a special outlet-pipe for the stagnant gases and re-introducing them tangentially into the chamber.

Th. Meyer fully discusses the removal of mist in a pamphlet, *Das Tangential-Kammersystem*, published at Offenbach in 1904, and reviewed in *Z. angew. Chem.*, 1904, p. 477; see also *Z. angew. Chem.*, 14 (50), pp. 1245-1250.

Grosse-Leege (Ger. P. 162218) describes a circular chamber with tangential introduction of the gases, narrowed towards the

exit-pipe for the gases, which is arranged sideways, so that the gases must travel all along the walls of the chamber. Steam-injectors are arranged so that they send out a steam-jet tangentially in the direction of the gaseous current. By means of a spout with perforated bottom, surrounding the top of the chamber, cooling-water may be run down the outer surface of the chamber.[1]

Mills-Packard water-cooled sulphuric-acid chambers have been installed by thirty different companies. The first two chambers were erected in 1913-14, and the number of chambers of this type has increased at the present time (June 1923) to one hundred and forty-three, with approximately one and a quarter million cubic feet chamber-space. The chambers have been erected in several countries, including New Zealand, and since the war the plant has made rapid progress on the Continent, where important installations are working.

These chambers have been built in three sizes, of 7330, 11,890, and 18,750 cub. ft. each. Plants composed entirely of Mills-Packard chambers have operated successfully at below 3 cub. ft. chamber-space. Combined plants of their small chambers with ordinary chambers are operating at from 5 to 10 cub. ft. chamber-space.

It has been found that, with efficient water-cooling, the wear and tear is very small. The original chambers after eight years' working require very little repair. The quantity of water employed on the outside of the chamber is increased or diminished according to the intensity of the reaction. The chambers may be constructed without any covering, but there is no difficulty about housing them, and it would probably be advantageous, where great changes in temperature are encountered, to cover them.

The control of the process is not more difficult than with the ordinary rectangular chambers, as any irregularity in working is easily corrected owing to the small distance the gases have to travel.

The chambers can be employed either in complete units up to twelve chambers in a set, or, in conjunction with rectangular ones, when they take the place of intermediate towers. It is

[1] *Z. angew. Chem.*, 1905, p. 1909.

claimed for these chambers that they possess the following advantages:

1. High production with low nitre consumption.
2. Low wear and tear of the lead.
3. First cost of construction per ton of acid produced reduced to a minimum.
4. Very small ground-space required.
5. Simplicity of construction.

The method of introducing the gases into the chamber is by a single inlet arranged at an angle of about 45° to the base, in such manner that the gases impinge directly upon the acid in the dish.

Tube rings are spaced at suitable intervals according to the size of the chambers (see Fig. 41*a*). The ceiling is dished in the smaller chambers, but a raised ceiling is used in the larger types. All ceilings are water-cooled.

The standard framework is of steel construction, but a number of chambers have been erected with wooden framework, and some with the main framework of reinforced concrete.

Harris and Thomas (B. P. 104461 of 1916) describe a chamber of circular construction which is provided with a pipe for admitting the gases tangentially near the bottom, so as to direct them round the walls, and with a central hollow column extending upwards from the pan and opening at the upper part into the chamber to form an exit-pipe for the gases. The central column may be cooled by means of weak acid or water directed against it, or by adjacent water-cooled pipes, and the last chamber of a series may be packed, and supplied with acid.

Welch (U.S. P. 1328552, assigned to The International Precipitation Co., 1920) claims that the efficiency of the chamber-process is improved by removing the mist formed in the first chamber by passing it through an electrical precipitator. The presence of the mist particles of nitrosyl sulphuric acid in the chambers tends to inhibit the completion of the reaction. Welch claims additional advantages as follows:

Circulation of the gases in the chamber by withdrawing the vapours at one end of the chamber and returning them (after they have passed through the precipitator) at the opposite end; and cooling of the gases so that the heat of the reaction does not raise the temperature above the optimum. Chamber-

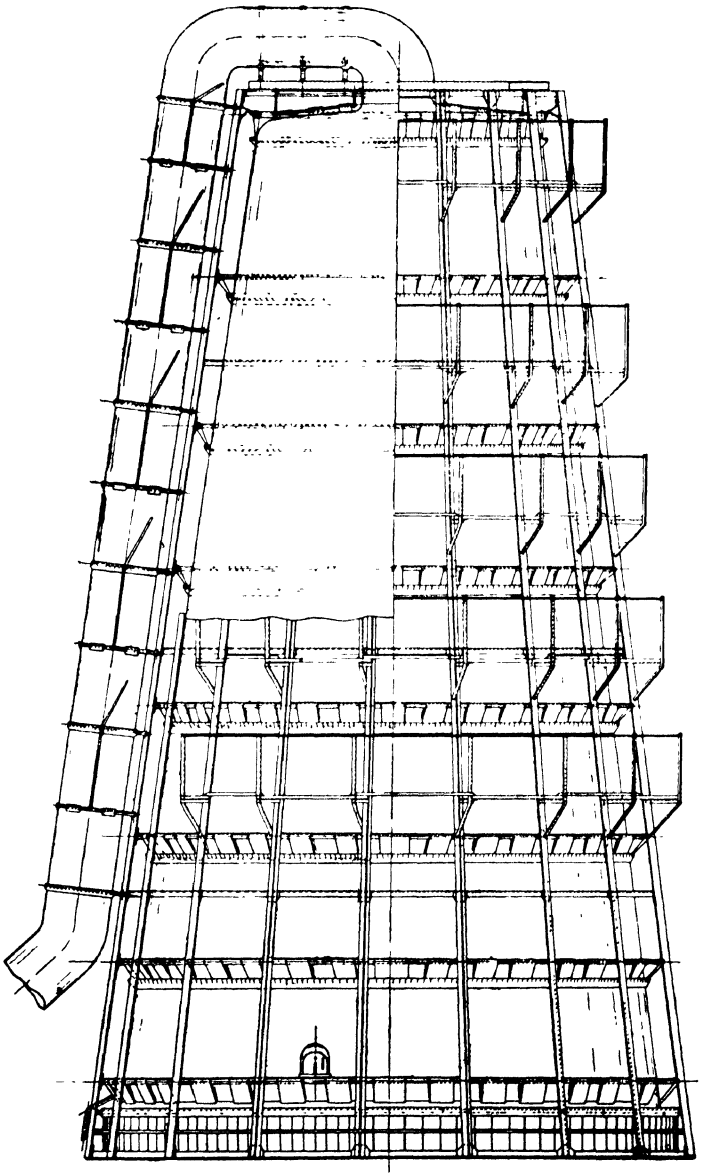


FIG. 41*a*.

acid flows through the precipitator, and the strong acid thus formed is fed to the Glover tower.

R. E. Dior (B. P. 164572 of 1920) describes a somewhat similar type of chamber. In a series, their size and height decrease in order, the tallest being connected with the Glover, and the shortest with the Gay-Lussac. They resemble in shape an inverted funnel, in which the sides of the upper part are more vertical than the sides of the lower part. The gases, which enter at the bottom and leave at the top, are caused to move spirally by placing the inlet and outlet tangentially to the circumference of the chamber. Water, steam, or dilute acid may be directed downwards by injectors placed in the roof of the chambers. Water is also caused to flow down the outside for cooling purposes.

Acid from the back chambers is conveyed to the earlier chambers, concentration of weak acids thus being accomplished.

Intermediate ("Reaction") Towers.

Another way of increasing the production of acid is the employment of special *mixing and cooling towers and columns* between the chambers, even the complete substitution of these towers for chambers. These "intermediate" or "reaction" towers have had the greatest success in diminishing the space required for the production of sulphuric acid.

One of the first attempts in this direction was made by Thyss (Ger. P. 30211) (see Lunge, second edition, pp. 378 and 379). As his system broke down completely after a short trial, it must suffice to say that Thyss employed lead towers, provided with a number of perforated lead shelves over which the gas had to take a zigzag course. These towers were not fed with any liquid, and consequently they must have become very hot and could exert little cooling action. The draught was very much impeded, and the lead quickly corroded. Moreover, these towers cost twice as much as an ordinary chamber producing the same amount of acid. Although the Thyss columns were both an economic and a technical failure, they proved that, even in such imperfect form, an intimate mixture of the gases and their contact with solid surfaces considerably accelerate the reaction.

Sorel[1] proposed to start with a small chamber. From this the gases passed through cooling-pipes and then through two or three towers, where steam was also injected, whilst acid of 142° to 150° Tw. was run down. The out-flowing acid was not to fall below 130° Tw.

Lunge's Plate-towers.—It is probably generally recognised that the object in question was first fully accomplished by Lunge's *plate-towers*,[2] in which he endeavoured to combine all the principles hitherto recognised as paramount in the manufacture of sulphuric acid. He formulates the theory of the chamber-process as follows:—By the action of nitrous acid (or anhydride)—or in the first part of the chambers nitric oxide, which acts as carrier of atmospheric oxygen—and water upon sulphur dioxide, nitrososulphuric acid is formed. This acid, which for the most part at once dissolves in the sulphuric acid already present, floats about in the chamber in the form of a fine mist. When it comes into contact with water, or, as is probably the usual case, with dilute sulphuric acid, a decomposition takes place by which sulphuric acid is formed, and all the nitrous acid is returned into the atmosphere of the chamber to recommence the action described above.

It is evident that all these reactions require, in the first instance, a most intimate and constantly renewed *mixture* of all the gases, vapours, and misty particles. In the ordinary large chambers a long course, a vast space, and a correspondingly long time are needed until the reactions are practically complete—that is, until nearly all the SO_2 has been removed from the gases. If it were only a question of a mixture of gases and vapours, probably very much less time and space would be required; but as both the nitrososulphuric acid and the dilute sulphuric acid, which are to act upon each other, are in the form of mist—that is, of minute *liquid* drops—they may travel for some distance side by side without coming into actual contact and reacting as they are intended to do. In many similar cases it has been found that simply mixing up the atmosphere in question is not nearly so efficient as presenting large *solid* (or liquid) *surfaces* against which the gaseous current

[1] *Cf.* his *Fabrication d'acide sulfurique*, p. 398, and *Z. angew. Chem.*, 1889, p. 279; *J. Soc. Chem. Ind.*, 1890, p. 181.

[2] *Z. angew. Chem.*, 1889, p. 385.

must strike in its progress. By the shock against these surfaces, and the loss of velocity which follows, and undoubtedly also by surface attraction, the misty particles, which would otherwise float about for hours, are condensed on those surfaces in larger drops or films, and then the mutual reaction leading to the splitting up of nitrososulphuric acid takes place at once. It is advantageous, therefore, to arrange a number of large solid surfaces in the path of the gaseous current, so that this current must continually strike against them and be constantly broken up into small parts and mixed again. (In this respect Ward's glass sheets (p. 52), running parallel with the gaseous current, were not properly disposed.)

There is, however, another condition to be realised for a proper working of the chamber-process. As will be shown further on, it is indispensable that the *temperature* of the chamber be kept sufficiently low to condense the requisite quantity of aqueous vapour into liquid water or dilute acid, sufficient for decomposing the nitrososulphuric acid. As the reactions in progress within the chambers produce a large quantity of heat, the process cannot go on without a portion of that heat being abstracted again, which in the ordinary system is done by radiation from the chamber-sides. The separation of the whole chamber-space into several smaller chambers acts favourably in this respect, as the ends of the chambers and the connecting-pipes act as cooling-surfaces; and Sorel (*supra*) proposed to increase this by arranging a set of cooling-pipes, which, however, would not be sufficient for the purpose. Lunge's plan is, however, different from anything previously proposed. He effects the necessary lowering of temperature, not by radiation or convection to the outer air, but from within by a shower of water or very dilute sulphuric acid. Thus several objects are attained at the same time. The temperature of the chamber atmosphere is reduced to the proper degree, part of the heat being used in heating and vaporising water. This water-vapour is just what is required for carrying on the chamber-process itself, and thus a saving is effected in the raising of steam for the purpose of supplying the vitriol-chambers. He also supplies water in a finely divided form, and exactly where it is needed for meeting and decomposing the nitrososulphuric acid condensing on the solid surfaces.

The cooling thus effected protects the apparatus against rapid deterioration, such as occurred in the Thyss plan (p. 66).

The "plate-column" or "plate-tower" invented by Lunge consisted originally of a large column of stoneware cylinders, filled with the plates forming the peculiarity of the invention. This is the construction employed for nitric and hydrochloric acid, but for the purpose of sulphuric-acid manufacture it is constructed with a leaden shell.

It is fully described and illustrated in Lunge's fourth edition, p. 659 *et seq.*

The difference in condensing-power between the "plate-tower" and a perfectly well constructed and packed coke-tower, or any similar apparatus, is due to the fact that the liquid within a coke-tower is never quite evenly distributed; there are always many places where it falls without meeting a piece of coke, and where, on the other hand, the gases find channels in which they can ascend some distance without getting mixed and coming into contact with liquid. Moreover, the individual gas-channels are too wide, and the inner portion of the gaseous current does not enter into reaction with the absorbing liquid. This is unavoidable, because the interstices between the pieces of coke are quite irregular. Coke-towers must therefore be made very wide and high, thus giving a long time and corresponding opportunities for the gases to mix and to enable them to come into contact with the liquid. In this way the reaction may be very complete at the end.

A plate-tower, in comparison with a coke-tower, does from ten to twenty times as much work in the same cubic space. It can therefore be made not merely much smaller in section, but also much lower in height, and the feeding-liquid requires correspondingly less pumping. A column of 40 plates would be only 18 ft. high. The above is a comparison between plate-towers and coke-towers; the difference between the former and empty chamber-space is much greater, as will be seen.

It is of special importance that the injurious action due to the reducing power of coke upon the nitrous gases (p. 53) should be avoided. Stoneware plates of proper quality are absolutely stable in the chamber atmosphere. They last, therefore, practically for ever; even if cracked they still continue in use.

When a plate-column is partly obstructed by muddy deposits, it is easily cleaned out by a thorough flushing with water, or, in bad cases, by removing all the plates.

Apart from the great difference in construction between the plate-towers and all previously proposed apparatus, there is an equally great difference in their mode of application. If the tower were left to itself, like Ward's or Thyss's apparatus (*supra*), the very completeness of the mixture produced therein would cause an intense chemical reaction, and consequently a very injurious development of heat. This is entirely avoided, however, by feeding the towers with a stream of water or dilute sulphuric acid, at such a rate that, by the vaporisation of water, the temperature does not rise above 70° or 80°. The intimate contact between gaseous and liquid particles within the plate-tower brings the cooling action due to the evaporation of water to its fullest extent, and at the same time the water required for the chemical reactions of the acid-making process is supplied without any extraneous production of steam or spray. The superfluous steam passes over into the next chamber or tower and does its work there.

In plate-towers there will always be a great excess of nitrous gas and of oxygen. There is, therefore, very little fear that the conditions for the formation of nitrous oxide, which would mean a waste of nitre, will be present, even when employing water for feeding them. These conditions can be avoided in any case by feeding the columns with sulphuric acid of sp. gr. 1·3 or upwards, since Lunge[1] showed that in this case no N_2O whatever is formed. In practice this dilute acid or chamber-acid is employed for feeding the columns.

The principal advantage of this system is that, like the Glover tower, it brings about the mutual action of the ingredients within the smallest possible space. It will be shown in Chapter II that 1 cub. ft. space in the Glover tower effects the formation of as much acid as at least 180 cub. ft. of ordinary chamber-space; and a similar difference may be looked for between the latter and towers interposed between the chambers.

As a practical way of applying the new system, Lunge[2] proposed the following plan:—

[1] *Ber.*, 1881, p. 2200; *cf. supra*, p. 258 of Vol. I.
[2] Lunge, 4th ed., p. 666.

"Considering that by far the greatest portion of the acid is made in the first part of the chamber, the back part is cut off altogether, which leaves behind the Glover tower a chamber of only about 50 ft. length. Behind this is placed a plate-tower of sufficient section for the amount of gas to pass through and 40 plates high (say 18 ft.). Then comes a small chamber, say 30 ft. long, again a plate-tower, a last chamber for drying the gases, and in the end a plate-tower serving as Gay-Lussac tower."

The question might be raised why Lunge did not propose to carry on the whole of the sulphuric-acid-making process in plate-towers or similar apparatus. A glance at the curves shown in Chapter III will show, however, that the first part of the first chamber is really very efficient, and with gases of a certain concentration a lead-chamber is possibly the cheapest apparatus for making sulphuric acid. As soon as the curves begin to bend towards the horizontal—that is, when the reactions become sluggish—it is time to liven them up by apparatus like the plate-towers. If these were used from the first, the heat would become excessive, and this would be very injurious both to the material of the apparatus and to the process.

The first factory which ventured to try "Lunge" towers was the old-established acid-works at Lukawetz, in Bohemia, soon followed by a factory at Valencia, in Spain (both in 1891), and by others in various countries. Of course, here and there difficulties were experienced, principally caused by the obstruction of draught. Thus in *Z. angew. Chem.*, 1895, p. 407, P. W. Hofmann alluded to a trial which failed because the holes in the plates, 8 mm. bore, became filled with liquid and thus stopped the draught. Lunge (*ibid.*, p. 409) completely refuted this objection, mentioning that already about 200 plate-towers were then at work, most of them with even smaller holes, and a large number with 8 mm. holes.

The part played by the Lunge towers in the manufacture of sulphuric acid has been discussed at length by Niedenführ in *Chem. Zeit.*, 1896, p. 31. According to him, plate-towers are not very well adapted for replacing the whole of the ordinary vitriol-chambers. The first part of the process is always best carried out in a single lead-chamber, as here the gases are sufficiently concentrated to react upon each other.

[In this view, as well as in all other essential points of Niedenführ's paper, Lunge fully concurred.] Here also the flue-dust and the excessive rise of temperature would act injuriously in a tower. Hence it is not advantageous to place a Lunge tower between the Glover tower and the first chamber, but it should be placed in the central or back part of the set of chambers. Even then the results obtained with these towers must and do differ at different works, according to circumstances, viz., the available chamber-space, the draught, the size of the burners and of the connecting-pipes, of the Gay-Lussac tower, and so forth. In some cases, the working-capacity of the tower is partly taken up in correcting some fault in the set of chambers to which it has been applied.

The Lunge tower cannot be substituted for a Glover tower, as the holes of the plates would be too quickly stopped up by flue-dust, and in washing this down the plates would easily crack. Niedenführ, however, recommends placing a few tiers of plates with ½-in. holes in the upper part of the Glover tower. He quotes a case where a Lunge tower was found specially useful in completely denitrating chamber-acid required to be entirely free from nitrogen compounds.

Especially good results have been obtained in a number of cases, personally observed by Niedenführ, where plate-towers were employed as auxiliaries to Gay-Lussac towers. They act not merely in promoting the absorption of the nitrous gases, but also in rendering the chamber-work much more regular, especially in places where the chambers are subjected to sudden changes of weather, gales, etc.

Niedenführ in the paper quoted above makes certain proposals for the erection of sulphuric-acid works, using a combination of chambers and plate-towers. His proposals are not quoted here, because they are rendered obsolete by recent experience, the result of which will be noticed in Chapter V, where a complete plan for this purpose will be given.

If plate-towers are to be combined with existing systems, it is of course necessary in considering their size and position to take existing circumstances into account, so that it is difficult to lay down general rules. Where new plant is to be erected, however, long experience has established certain rules.

Niedenführ proposed to replace the lead-chambers altogether

by Lunge towers, taking care to erect the first part with as little loss of draught as possible, and to remove the heat of reaction to the necessary extent. This is done by making the reaction-towers, which immediately follow the Glover towers, of a wider section, and providing them with a very efficient feeding arrangement. The last towers must be made narrower than corresponds to the volume of gases passing through the first towers, in order to increase their speed and thus by the extra

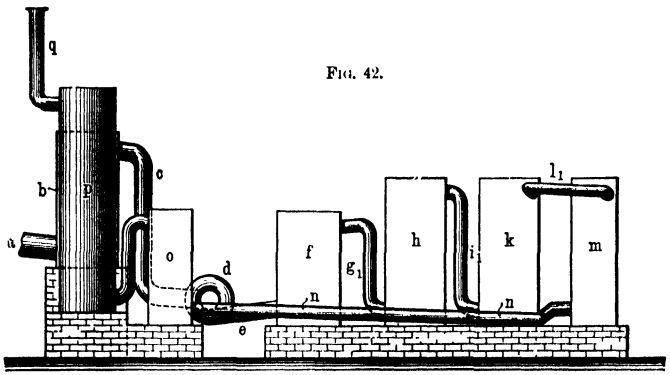


FIG. 42.

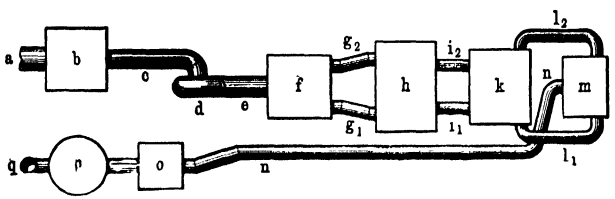


FIG. 43.

friction promote the reaction. The plate distances in these final towers must be kept smaller than in the first towers.

Niedenführ believes the following arrangement to be suitable for working with towers alone, without chambers (Figs. 42 and 43). The burner-gases pass through *a* into a preliminary tower *b*, and through *c* to the fan *d*, which conveys them through *e* to the denitrator *f*. This apparatus is fed with nitrous vitriol and warm water or dilute acid so as to furnish acid of 54° Bé. (= 119½° Tw.). It also receives the nitric acid required for making up the losses. It is packed like a Glover tower, preferably with dish-like packing. Part of the acid made here is employed for feeding tower *b*. This

denitrating tower is constructed on the same principle as Niedenführ's ordinary Glover towers, viz., with an interruption of the packing intended to facilitate the cleaning of the bottom part, and with sufficiently large openings for the passage of the gas. The acid with which tower *b* is fed is concentrated, and the gases are purified and partly cooled so that they may pass through the fan without trouble. They effect the denitration in *f* and then pass through g_1, g_2 to the first plate-tower *h*; pipes g_1, g_2, as well as the pipes i_1, i_2, are provided with steam-pipes. In *h* and *k* the gases enter at the bottom and issue at the top, but in the last reaction-tower *m* they enter at the top and leave at the bottom through *n*. This arrangement has been found to give the best result. The gases now pass into the first Gay-Lussac tower *o*, containing 16 layers of 9 plates each, then into the second Gay-Lussac *p*, packed with coke, and finally through *q* into the open air.

The acid coming from the first Glover tower *b* is freed from most of its impurities by means of a cooler.

If the same production is to be attained by a combination of chambers and plate-towers, this can be done as shown in Figs. 44 and 45.

From the Glover tower *a* the gases pass into a lead-chamber *b* provided with air-cooling shafts c_1, c_2, c_3. In this case no fan need be employed, but the gases must have a sufficient upward draught from the burners to the Glover tower and from this to the chamber *b*. Now come the two plate-towers *d* and *e*. These, as well as tower *a*, may be placed at a lower level than the chamber, which is all the better for the work. At *e* the gases are passed in at the bottom and out at the top, through *f* into the first Gay-Lussac tower (a plate-tower) *g*, then into the coke-packed Gay-Lussac *h*, and through *i* into the open air.

In a similar way large systems can be constructed with one chamber and a suitable number of Lunge towers. Niedenführ does not, even for the largest systems, propose more than two chambers, placing between them a very wide plate-tower with great distances between the plates. All the remaining towers are behind the second chamber. In Chapter V plans will be given for such a combination.

Other Apparatus on the Principle of Plate-towers.—Plate-

towers are sometimes blamed for impeding the draught, and one of the objects aimed at by some of the inventions described is to avoid any such impediment (see below). This objection to plate-towers is groundless, however, in view of the ease with which the chamber-draught can be regulated by a fan.

It should be borne in mind, too, that the efficiency of an

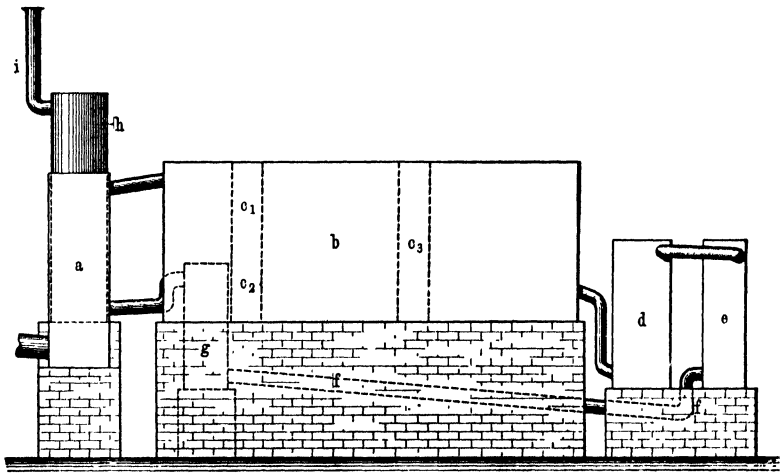


FIG. 44.

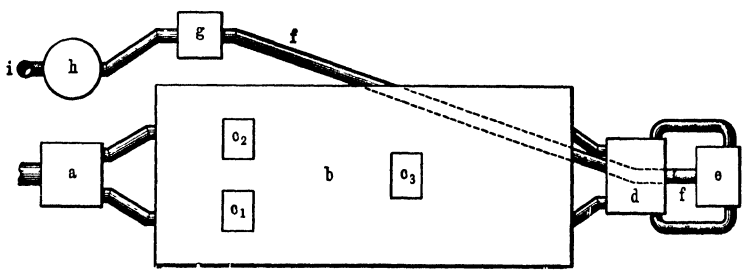


FIG. 45.

apparatus of this kind is practically proportional to its draught-impeding capacity.

Hacker and Gilchrist (B. P. 15895 of 1893) use a number of horizontal lead tubes, running from one side of the tower to the other and alternating in position. These towers, which they call "pipe-towers," are fed with water or sulphuric acid. Cold air is drawn or blown through the pipes. A paper in *J. Soc. Chem. Ind.*, 1894, p. 1142, contains a detailed account

of this system, and in the discussion several speakers threw great doubt upon its efficiency. This criticism is hardly justified, as the introduction of these "pipe-towers" into many American factories seems to show. Another paper on these towers was published in *J. Soc. Chem. Ind.*, 1899, p. 461, in which some improvements in details are indicated. A similar plan is that of Winsloe and Hart (B. P. 20142 of 1901), who employ perpendicular air-cooling pipes in a shaft connecting two chambers.

Hart and Bailey[1] describe a plant similar to Hacker and Gilchrist's pipe-towers, only of somewhat larger dimensions. They found a cooling-action of nearly 40°, an increase of production of 60 per cent., and a decrease of nitre of from 3·5 to about 2·0 per cent. All this agrees perfectly with the views first clearly stated by Lunge. The acid scrubbed out in their pipe-towers contained practically no "nitre."

Rabe[2] describes a feeding-arrangement with automatic movement and internal cooling-arrangements for these towers.

W. Wyld and S. W. Shepherd (B. P. 839 of 1915) arrange the packing, consisting of strips of glass, or other suitable material, within chambers of towers of circular transverse section. This has previously necessitated the employment of glass strips of varying lengths, as the strips have been arranged in parallel formation across the interior of the tower, and have, of necessity, had to be of decreasing length as they become further away from the diameter. Furthermore, particularly in instances in which the strips are composed of glass, the internal diameter of the tower is confined to certain limits, as the strips of glass are not sufficiently strong to span more than a certain diameter, and it is frequently desirable to construct a chamber or tower of greater diameter than this. An advantage of Wyld and Shepherd's method of packing lies in the fact that the diameter and capacity of the tower or chamber can be considerably increased without involving risk of breakage of the strips when made of glass (see B. P. 19001 of 1906 and 8317 of 1907, p. 240).

A further advantage is that its arrangement tends to direct

[1] *J. Soc. Chem. Ind.*, 1903, p. 473.
[2] *Z. angew. Chem.*, 1903, p. 437.

the gases towards the outer circular cooling-wall of the chamber.

Incorporated centrally within the tower or chamber is a pillar or support, conveniently of circular transverse section, and disposed concentrically with the internal circular surface of the chamber-wall. The external surface of the central supporting member and the internal surface of the outer wall of the chamber are each formed with ledges or other means of support, upon which the extremities of the strips of glass or other suitable material may be placed, and the strips of glass are then assembled so that they radiate from the central supporting member to the outer wall, the spaces between the strips increasing from their inner to their outer extremities.

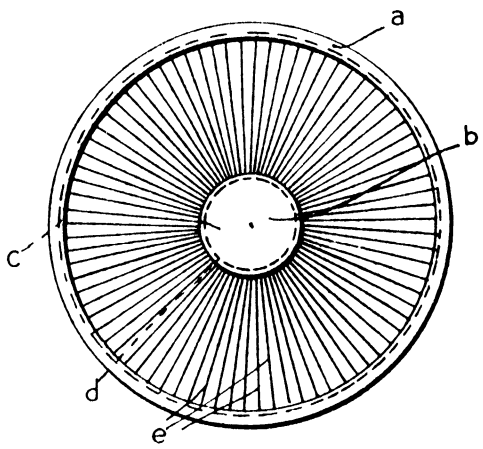


FIG. 46.

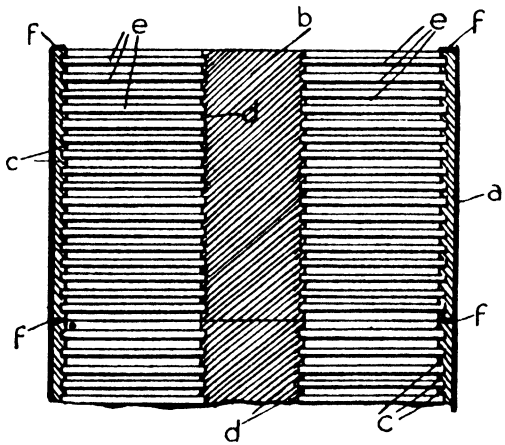


FIG. 47.

Fig. 46 is a section plan of a tower illustrating one arrangement.

Fig. 47 is a part sectional elevation of the tower shown in Fig. 46.

Fig. 48 is a sectional plan of a tower showing a modified arrangement.

In the drawings, *a* is the outer wall of the tower or chamber, in the centre of which is placed a pillar or support *b*, the external surface of the central supporting pillar *b* and the internal surface of the outer wall of the chamber *a* being each formed with ledges *c*, *d*, as shown in Fig. 47 ; the strips *e* of glass or other suitable material are assembled to rest upon the ledges *c*, *d* in such a manner that they extend from the central member *b* to the outer wall *a*.

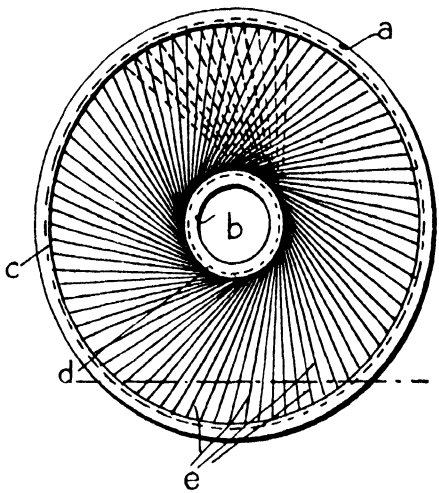


FIG. 48.

The glass or other strips *d* may be arranged radially as shown in Fig. 46, or may be arranged tangentially to the central supporting member as shown in Fig. 48, for which purpose they are slightly longer than the radial distance between the supporting member *b* and the outer wall *a*. The glass strips *e* are disposed edgewise, and the layers are repeated at close intervals throughout the entire length or height of the tower or chamber. By arranging the strips of alternate layers tangentially inclined in opposite directions as shown in Fig. 48, the divided films of gases passing through one layer of strips are cut transversely by the next layer of strips, and thus a particularly satisfactory subdivision of the gases and intimate contact with the surfaces is effected.

A column 15 ft. high by 5 ft. diameter, packed as described, when placed between No. 1 and No. 2 chambers shows a production of acid equal to 0·5 cub. ft. space per lb. of sulphur per 24 hours. When working between the second and third chambers, they give a make equal to 4 cub. ft. of space per lb. of sulphur per 24 hours.

Replacing the Lead-chambers entirely by other Apparatus, Towers, etc.

After all that has been stated on the possibility of carrying out the manufacture of sulphuric acid by the ordinary reaction where nitrous gases are the oxygen carriers, but in a much smaller space than is used in lead-chambers, the question naturally arises whether the lead-chambers cannot be *completely* replaced by apparatus of greatly reduced cubic space. Mention has already been made of proposals in that direction (*cf.* p. 73) which were prompted by the success of the plate-towers. Long before this, however, inventors had attempted to abolish the lead-chambers. The proposals made in this direction in former and in recent times are enumerated below.

MacDougal and Rawson (B. P. of 1848) conduct sulphur dioxide and air through nitric acid contained in a Woulfe's bottle, in which sulphuric acid and nitrogen peroxide are generated; the latter, with the excess of air, passes through several vessels filled with water, in which the nitric acid is regenerated.

Hunt (B. P. of 1853) conveys a mixture of sulphur dioxide and air through a tower filled with pebbles, down which nitrous vitriol continuously trickles. This principle had already been proposed by Gay-Lussac, and it is actually carried out in the Glover towers, so far as it is practicable—that is, by conducting the escaping gases into lead-chambers.

Durand, Huguenin & Co. (Fr. P. 205589 of 1890) pass a mixture of sulphur dioxide and air through tanks charged with nitric acid or solutions of nitrous products. The tanks alternate with condensing-towers. The liquids are made to flow systematically through the apparatus in such a manner that at last concentrated sulphuric acid, free from nitric or nitrous acid, is obtained. The above-mentioned gaseous mixture is produced by passing compressed air into sulphur- or pyrites-burners, thus also obtaining the pressure necessary for forcing the gas through the liquids contained in the tanks.

Barbier's apparatus for manufacturing sulphuric acid (B. P. 12726 of 1892; Ger. P. 69501) consists of six towers, arranged in steps, packed with hollow pieces of sandstone, quartz, or the like.

Heinz and Chase (U.S. P. 875909) pass the burner-gases first through a Glover tower, then through flues, where steam and nitric acid are admitted and part of the sulphuric acid is made. After drying and purifying, the gases pass through a contact apparatus and then through a Gay-Lussac tower.

The Chemische Fabrik Griesheim-Elektron (Ger. P. 226610) have found that the chambers can be entirely replaced by towers, provided that the oxidation of SO_2 by an access of nitric acid is such that none of it can get into the nitre-recovery towers. The process differs from that of other tower systems in that the formation of sulphuric acid is locally separated from that of nitric acid. It has also been found that the complete oxidation of nitrogen oxides to HNO_3 requires a certain time (at least four minutes) on account of the great dilution with inert gases. A pyrites-burner of a capacity of 10 tons and yielding 40 cub. m. burner-gases per minute must, therefore, be furnished with a nitre-recovery apparatus of at least 160 cub. m. capacity. This system is carried out as follows :—The pyrites-burner gases pass first through a Glover tower and then into the oxidising-towers, fed with nitric acid 30° to 35° Bé., where the SO_2 is almost instantaneously oxidised. From the towers runs an acid containing 50 to 54 per cent. H_2SO_4 and about 1 per cent. HNO_3, which is brought back to the Glover for complete denitration and concentration. From the oxidising-towers the gases pass through several towers, fed with mixtures of nitric and sulphuric acid of various concentration, and here nitric acid, of a quality suitable for the process, is recovered. For working up the SO_2 from burners charged with 10 tons pyrites, only 200 cub. m. of total reaction space is required, viz., 30 cub. m. for the oxidation of the SO_2 and 170 for the recovery of the nitric acid. Their additional Ger. P. 229565 suggests working at temperatures of 35° to 65°. Above 65° part of the nitric acid distils off without having acted as oxidiser, and below 35° the reaction goes on too slowly. This regulation of temperature is most easily attained by employing acid of about 50° for feeding the oxidising-towers. Their B. Ps. are 20401 and 23442 of 1909; Belg. Ps. 218994 and 219727; Fr. P. 406641 and addition; Ital. P. 37914; Austr. Ps. appl. A 66331 and 74991; Norw. Ps. 20774 and 25381; Swed. Ps.

29988 and 30825 ; Spanish Ps. 46267 and 46459 ; Austral. P. 17739 ; applications made in Russia and the United States.

The Erste Oesterreichische Sodafabrik at Hruschau and C. Opl (B. P. 20171 of 1908 ; Fr. P. 394739 ; Ger. P. 217036 ; U.S. P. 1012421) describe an arrangement for producing sulphuric acid without chambers, on which Opl reports in *Z. angew. Chem.*, 1909, p. 1961 *et seq.* He started with the well-known theory that the chamber-process for producing sulphuric acid may be considered as a contact process in which nitrososulphuric acid acts as catalyser for the combination of SO_2, O, and H_2O.

Opl[1] states that in his system usually six towers are employed, the three first forming sulphuric acid, similar to Glover towers, and the three last retaining the nitrous gases in strong sulphuric acid, like Gay-Lussac towers. The gases leaving the last tower, which contain 6 per cent. oxygen and 1-5 gram SO_3 per cubic metre, are aspirated by an ordinary low-pressure Kestner fan and forced into a box filled with coke, where the last traces of SO_3 are retained.

The water required for the formation of sulphuric acid is supplied in the second, third, and fourth towers, the fresh nitric acid generally only in the second tower. The acid is moved about by means of emulsifiers ; that which is running out of the sixth tower through an overflow, is fed into the first tower ; the acid from the fifth tower goes into the second, and that from the fourth tower into the third. Finally, all the acids go into the first tower, and from this through coolers into store-tanks. The acids supplied to the three last towers are also cooled, in order to carry away the injurious heat of reaction. Owing to the better utilisation of space, the acid-forming process requires only about twenty minutes, against four to six hours in the chambers. The reacting space is about one-tenth of that in the chambers. For the daily production of 18 tons sulphuric acid of 60° Bé., six towers of 3 m. × 3 m. section and 12 m. high are required ; that production requires 12 tons pyrites, 4 kilowatt power, 4000 cub. m. air compressed to 2 atmospheres, 160 kg. nitric acid 36° Bé., about 300 cub. m. cooling-water, and three men's work per shift (inclusive of the pyrites-burners).

[1] *Chem. Ind.*, 1914, p. 523.

According to the *Alkali Report*, No. 56 for 1919, the Opl plant works with a very small space available for the process-gases and liquid acid. From information received by the Chief Inspector from Chance & Hunt, Ltd., the rates of conversion in an Opl set compared with a Glover tower are as follows:—

	SO_2 burner pipe.	SO_2 tower exit.	Per cent. of total SO_2 removed.
Glover tower . .	5·89	5·34	8·8
First tower Opl set .	7·75	6·7	13·5

The gases pass through the Glover tower in about forty seconds, and through No. 1 tower of the Opl set in about two minutes, so that the reaction is about three times as rapid in the Glover as in the first tower of the Opl, and is much more vigorous in the second and third Opl towers than in the first.

It is interesting to note the wide difference in speed of reaction in the two towers, but not very surprising when one remembers that all the nitrous gases supplied to the ordinary chamber system enter the Glover tower in the nitrous vitriol from the Gay-Lussac towers, or from the nitric acid generated in the potting ovens, which at once proceeds to act upon the burner-gases, whilst in the Opl plant only a portion of the nitrous vitriol enters the first tower, and the fresh supply of nitric acid enters the system at a later stage of the process. Hartmann[1] enumerates the advantages of the tower system as follows:—1. Less cost of plant. 2. Less ground space. 3. Easy supervision of the plant. 4. Easy superintendence of the working. 5. Production of all the acid at a strength of 60° Bé. 6. Lower cost of production than that of the lead-chamber process. The first experimental plant was erected in Hruschau in 1908, a larger plant in 1909, a third in 1910, and a fourth in 1911. Many other units have been erected in Austria and Sicily, and three are at present in use in England (1923).

Hasenclever, *J. Soc. Chem. Ind.*, 1911, p. 1292, reserves his judgment upon this (as well as on the Griesheim) plan; it

[1] *Z. angew. Chem.*, 1911, p. 2303.

remains to be seen whether the saving effected by smaller capital charges will not be counterbalanced by increased working expenses and repairs. The working requires, as he points out, careful supervision, as the consumption of nitre easily becomes heavy. In addition, the acid, through being continuously in contact with the packing material of the towers, will probably become more and more impure, even if the burner-gases are subjected to a preliminary purification.

The advantage claimed for the Opl process, that all the acid is obtained at a strength of 60° Bé. or 142° Tw., cannot be taken into account, as this result can be obtained with the chamber-system as well; and the Opl process has the drawback that all the acid comes out in an impure state, like that of Glover-tower acid. The question of wear and tear cannot be settled up to the present, but this item is likely to be somewhat higher in the Opl system than in the lead-chamber system. One circumstance is undoubtedly in favour of the Opl system, viz., that it requires less ground-space than the chamber-system; and where the purity of the acid is of no consequence, there is the advantage in the Opl system of smaller working expenses.

The discussion on the Opl process is continued by Hartmann [1] and Meyer.[2]

The writer found the following system to give satisfactory results. Fig. 49 shows a plan, and Fig. 50 the elevation of a plant for the production of 120 tons of 146° Tw. acid per week.

The towers 1 to 10 are erected upon a reinforced-concrete platform A, about 10 ft. above the ground, upon which also ample cooling-troughs B for the acid are provided.

The towers are 20 ft. high by 6 ft. square in section, and are packed according to Wyld and Shepherd's method as described on p. 76. Acid is circulated down the whole of them by any well-known means; no overhead storage-tanks are necessary, the elevators being arranged in duplicate. The acid leaving towers Nos. 1 and 2 is transferred to Nos. 9 and 10; that from Nos. 2 and 4 to Nos. 7 and 8; that from No. 5 to No. 6; and *vice versa*.

[1] *Z. angew. Chem.*, 1912, p. 817.
[2] *Ibid.*, p. 203 and p. 1426.

Owing to the enormous amount of contact surface possible by this type of packing, the plant occupies very little ground-space, and the production of acid is equal to a chamber-space of 0·6 cub. ft. per lb. of sulphur per 24 hours. The surplus acid is removed from No. 1 tower at 130° Tw., and is free from nitre. Water is fed on the top of the various columns, no steam- or water-sprays being necessary.

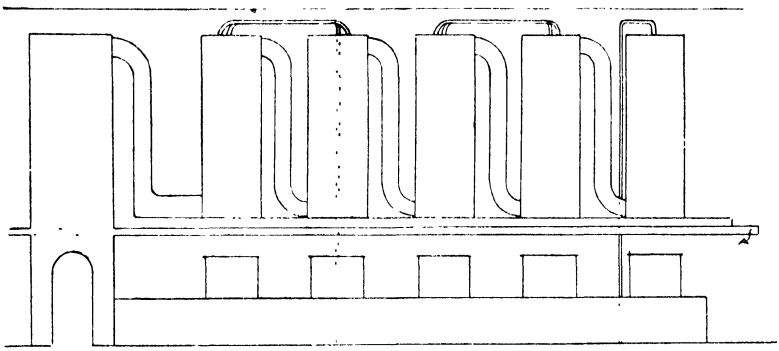


FIG. 49.

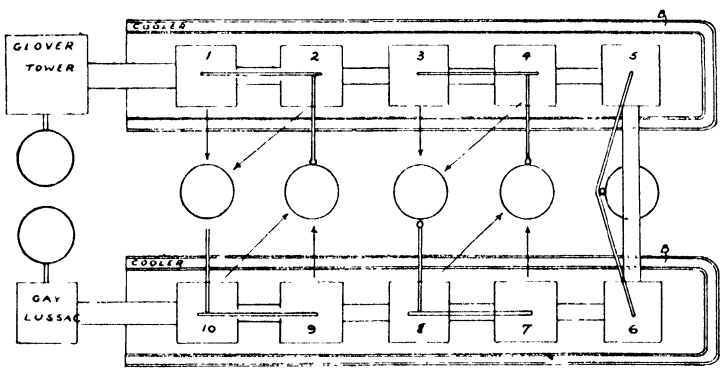


FIG. 50.

A fan is placed between the Glover and No. 1 tower, and a slight gas-pressure is maintained in the whole system.

E. W. Kauffmann (Ger. P. 226219) passes the burner-gases first through a dust-chamber with horizontal flues, and then, by means of a fan, into an iron tower lined with brickwork, where the necessary water and nitrous gases are introduced, and which is kept at 150° to 200°. The supply of water is regulated so as to produce acid of at least 142° to 151° Tw. (78 to 82 per

cent H_2SO_4). The gases coming out of the tower pass through a cooler and into a Gay-Lussac tower. The nitrous vitriol produced here is denitrated in apparatus similar to the old "steam columns" (*vide infra*), from which the nitrous gases re-enter the reaction-tower. This system also demands less ground-space than ordinary chambers, and furnishes acid of high concentration.

Fels (Ger. P. 228696) employs, behind the Glover, a series of horizontal cylinders with central shafts and agitating-blades, which cause a thorough mixture of the gases with each other and with the bottom-acid. The gases, which enter the cylinders in the centre and leave them at the top, are driven through them by a fan, placed behind the Glover; the acid formed runs through them all in the opposite direction, any excess of it being removed by U-shaped overflows. This method makes it possible to work with an excess of nitrous gases.

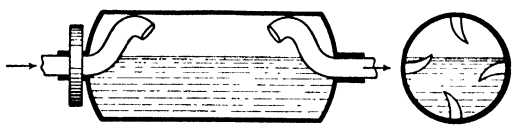


FIG. 51.

Wentzki (Ger. P. 230534) employs several horizontal revolving cylinders in series. The gases are passed in and out through hollow axes, which project only a short way into the cylinders and are bent upwards there, as shown in Fig. 51.

On the inside walls of the cylinder longitudinal bent shovels are placed, which, during the revolution, raise up the liquid, keep it permanently agitated, and throw it against the walls. To start the process the first cylinder is charged with nitrous vitriol or with a mixture of sulphuric and nitric acids. The other cylinders contain sulphuric acid. The burner-gases, propelled by a fan, enter the first cylinder, where they are partly converted into sulphuric acid. The nitrous gases, evolved here, travel along with the remaining gases and are retained in the second and third cylinders. The acid in the first cylinder is gradually denitrated and the contents of the second are changed into nitrous vitriol, and so forth. The same inventor (Ger. P. 238960) describes[1] the same process, carried out in a series of cylinders filled with a horizontal revolving stirring-apparatus.

[1] *Z. angew. Chem.*, 1911, p. 2440.

Petersen[1] proposes, in place of towers, to pass the burner-gases through a series of shallow lead boxes of 30 cub. m. connected by pipes, and rising behind one another. They are provided with perforated false bottoms, and packed above this with quartz. The first two boxes contain nitrous vitriol, the others sulphuric acid of sp. gr. 1·6 to 1·7. A fan draws the gases, cooled to 50° in a special cooler, through the acid in these boxes. In the first of these the SO_2 is at once transformed into H_2SO_4; the second prevents any escape of SO_2, and the evolved NO is absorbed in the third and fourth boxes. Acid of sp. gr. 1·6 is most suitable, as it readily absorbs nitrogen oxides, and is equally easily denitrated. Water is added in the gas-cooler or in the first box to maintain the sp. gr. at 1·6. The inventor also proposes another system consisting only of two boxes completely filled with quartz, and provided with short lead baffles projecting down from the lid. The acid, as it flows through, fills these boxes completely, and the gases pass horizontally through, so that less pressure is required than in the first system. His third system has only a single box, but is otherwise like the second system.

His patents are: B. Ps. 15406 of 1907, 21346 of 1907, 27738 of 1907; U.S. Ps. 899898, 899899, 904147; Fr. Ps. 378454, 382262.

Burckhardt (B. P. 29568, 1912; Ger. P. 259576; Fr. P. 452682) passes the hot burner-gas upwards in a tower containing a number of superposed pans filled with dilute sulphuric acid. The acid is concentrated, and the gases are cooled and saturated with aqueous vapour. They then pass over a series of pans filled with nitrous vitriol. The sulphuric acid formed in these is run into a dividing apparatus which delivers it to the first tower. The remaining gases go through a Gay-Lussac tower.

Heinz (Ger. P. 264640) employs a series of reaction towers, partially or entirely filled with packing materials, with alternately narrower and wider interstices, down which nitrous vitriol runs. Between the two last towers one or more empty towers may be placed, in order to diminish the velocity of the gases.

Steuber & Co. (D. R. G.-M. No. 541504) line the towers

[1] *Chem. Zeit.*, 1911, p. 493; *J. Soc. Chem. Ind.*, 1911, p. 681.

with stones, the inner faces of which are made slanting. This diverts the acid running down towards the interior of the tower, so that the cemented joints of the stones are not hit by it, and also prevents the acid from leaking out.

J. Mackenzie (B. P. 19084 of 1913) employs a series of long tunnels, made of acid-resisting bricks or blocks, in which are placed lead spouts lined with acid-proof bricks. The tunnels are provided at suitable intervals with tuyères for introducing acid, sprayed in by centrifugal pumps or otherwise, preferably taken from the same tunnel, whereby the whole tunnel is filled with a strong rain of acid through which the gases must pass, whilst sulphuric acid is made and condensed.

Volberg (Ger. P. 265724) arranges the packing of towers, etc., so that the single successive layers, *e.g.* of fireclay cylinders, are out of line with those above and below them. Each cylinder is filled with coke or charcoal in such a way that there is always sufficient space for the gases to pass through. This avoids the lack of uniformity in the channels for the gases.

W. Fulda (U.S. P. 1048953 of 1912) treats the burner-gases with nitric acid. The reduced nitric acid is then regenerated by passing it down a number of oxidising towers.

Carmichael and Guillaume (B. P. 15679 of 1913) employ a series of towers which are alternately empty and packed, so that the gases, after passing a tower filled with packing, can expand again in the next empty tower.

S. J. Tungay (B. P. 2408 of 1913, Ger. P. 267138, and Fr. P. 453733)[1] gives some details of the Duron system of intensive working in the production of sulphuric acid. The Duron tower system consists of six towers varying in shape. Tower I brings all the acid produced to a uniform concentrated state; Tower II works similar to a Glover tower; Towers III and IV are those where the actual manufacture of acid takes place; Towers V and VI are Gay-Lussac towers.

The acid during course of manufacture is lifted to the towers, without the medium of any reservoirs or tanks, by means of centrifugal pumps and endless acid-elevators, and not, as in the case of other tower systems, by using acid eggs which, he states, gives a very poor yield, and shows considerable installation costs.

[1] *Chem. Age*, 1922, **6**, 831.

The gases are spread over the whole section by means of a special system, avoiding the long and complicated pipes which is one of the drawbacks in many other systems of tower installation; and with these short connections the temperature necessary for the reaction is maintained. In addition to the working economy, this system offers a very considerable saving in the cost of installation, owing to its exceedingly compact form.

Of the six towers described, two must be protected, whilst the remaining four can be erected in the open. All the towers are slightly conical in form, following the ordinary factory chimney, and their stability is, in consequence, such that outside supports are rendered unnecessary.

It is estimated that the ground-space required by the Duron system is only one-quarter that required by a chamber-plant having the same effective capacity.

By means of an exhauster, U. Wedge (U.S. P. 1104590) passes the burner-gases, after they have left the Glover tower, through several rows of lead towers of about 10 superficial ft. section and 70 ft. high. The gases enter alternately at the top and at the bottom, whereby they are well mixed and produce a great deal of sulphuric acid. The steam present in excess is used up so quickly that the gases, after leaving the last tower, may be still utilised in ordinary chambers for the production of sulphuric acid. In a plant constructed in this way, the gases leaving the burners had a temperature of about 620°, and on coming out of the Glover, 135°. After passing through eight rows of nine towers each, altogether seventy-two towers, their temperature had fallen to 88°.

Littmann (Ger. P. 281005) employs a series of towers filled with pipes, and provided with branch pipes by which connections are made between the different towers, *i.e.* from the bottom of one tower to the top of the next. According to his Ger. P. 281537, the pipe-towers are placed in step formation, the back wall being smooth, and the steps, which may be three in number, placed on the opposite side, their diameter decreasing from the bottom upwards. The gases are passed into the top of the tower and a connection is made from the top to the lowest part of the pipe connecting two towers. In the uppermost intermediate pipe there is a slide for regulating the flow

of the gases. Ring-shaped vessels containing cooling-water are placed over the recesses formed by the steps, and in case of need the water may be made to run over the sides of the step-tower.

Hartmann (Ger. P. 282747) places, between the reaction towers and the Gay-Lussac tower, a tower filled with coke, stoneware packing, etc., which may be fed with sulphuric acid, for the purpose of condensing the acid fogs. According to the Ger. P. 284636 of Hartmann and Benker, they employ six towers; the first forms with the fifth, and the second with the last tower, closed rings for feeding with acid. The towers are packed with fireclay materials, *e.g.* Glover rings. Towers 1, 2, and 3 serve for producing acid; the acid fog carried away by the gases is partially retained in tower 4; tower 5 serves as the principal Gay-Lussac. The crossway connection of tower 1 with 5, and tower 2 with 6, allows the strongly nitrous acid from 5 to get to 1, and thus produces an increased formation of sulphuric acid.

Schliebs (Ger. P. 287589) places an "equaliser" behind one or all towers in a tower system. By this means the gases may be returned to the towers by a circular path.

According to U.S. P. 1151294 of Schliebs, the reacting gases are passed through a succession of towers, with a separator interposed between adjacent series, and a portion of the uncondensed gases is returned from each separator, through a connection furnished with draught-producing means, to the preceding series of towers.

Fr. Curtius & Co. (B. P. 28550, 1913; Ger. P. 287784 and 295708) pass the gases in the cold state into the tower system. Either the first tower, from which all the acid produced is taken, is fed with a comparatively small quantity of nitric acid or nitrous vitriol; or else the first tower is fed exclusively with the acid from the other producing-towers, which is poor in nitrous compounds and strongly concentrated, but not with nitrous vitriol from the Gay-Lussac towers. Thus, in spite of the low temperature of the gases, sulphuric acid of 50° to 60° Bé., free from nitrous compounds, is obtained. This new style of working is especially advantageous for burner-gases which have cooled down whilst being purified. The first tower, from which all the acid produced is taken, and which is made

considerably larger than usual, may be packed with coke, which is much cheaper and has a much greater surface than rings or stones. In a plant of six towers, all the acid produced in towers Nos. 2 to 4 is put on to tower No. 1, where it is denitrated and runs off as acid of 60° Bé. Towers 5 and 6 act as Gay-Lussacs. The nitrous vitriol from No. 6 goes to No. 5, and, together with the acid from this tower, to No. 2, or else directly from No. 6 to No. 2.

Two methods of working are described:—(*a*) Tower 8 (Fig. 52) is sprinkled with acid from the Glover, and the product, together with acid from the other towers, is conveyed to No. 1, where it is denitrated. Some of the denitrated acid is removed, and the rest is brought back to No. 8; acid flows between Nos. 2 and 7, Nos. 3 and 6, Nos. 4 and 5, in both

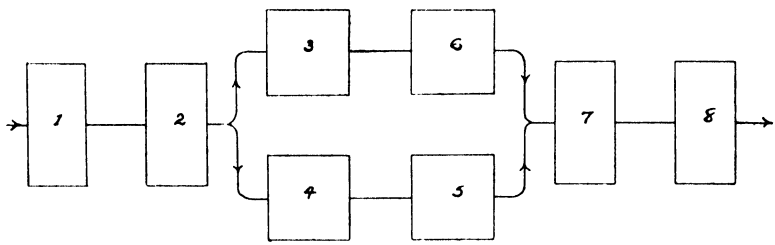


Fig. 52.

directions. (*b*) Tower 8 receives the Glover acid, and the product is conveyed to Nos. 7, 2, and 1 in succession, the acid from the other towers also passing to No. 1, where the whole is denitrated. Towers Nos. 3 and 6, and 4 and 5, work in closed circuit.

W. H. Waggaman (B. P. 101408 of 1916; U.S. P. 1185029) does not propose to do away with or modify the Glover or Gay-Lussac towers at present employed, but suggests the substitution of two or more lead pipes made in the form of spirals, for the ordinary chambers. Pipes having a diameter equal to that of the flues used in connecting the chambers in the ordinary chamber-process are best suited for the purpose, and two are usually sufficient to replace the chambers of a set.

The upper end or gas-entrance of the first spiral is connected directly with the Glover tower of the usual type. The lower end or exit of the spiral is connected with the lower end of a second spiral. The lower ends of both spirals are

connected with an acid tank by a common tube. The exit-end of the second spiral is connected with the lower part of the Gay-Lussac. Water-sprays control the temperature of the reacting gases.

The operation is as follows:—Hot gases from the Glover tower enter the first spiral, and are led downward by fan draught. The gases which still remain are then drawn through the second spiral, which can be heated if necessary by warm water. The resistance of the hot gases to the downward pull in the first spiral, and the resistance of the cooler gases to the upward pull in the second spiral, coupled with their constant change in direction, mixes them thoroughly, and brings about the necessary reactions in the shortest time and within the smallest chamber-space. Moreover, the immense amount of surface exposed by the spirals makes it possible to control the temperature of the gases within the most favourable limits for the efficient and economical production and precipitation of sulphuric acid.

The invention of E. L. Larison of the Anaconda Copper Mining Co. (U.S. Ps. 1342024 and 1334384)[1] describes what is known as the "packed-cell" process, which is a nitration process in which acid-sprayed packed towers, or "cells," are used instead of lead-chambers. The reaction spaces resemble the Opl process to some extent. For the operation of the process a specially designed "packed-cell plant" is needed.

The plant consists of the following:—

(1) A Glover tower of conventional design.

(2) A series of packed cells, or towers, built *en bloc*, exterior walls as well as interior walls of acid-proof masonry, the whole structure built in a lead pan, and the towers packed with chequer-work brick; the gas to take an alternately downward and upward course in passing though the cells; and each cell provided on the top with acid-distributing apparatus.

(3) Gay-Lussac towers built *en bloc*, but as a separate structure from the packed cells. Construction similar to that of the latter structure, with the exception of provision of a gas downtake (unpacked) between the Gay-Lussacs.

After experimenting on a small scale with this process a plant of about 20 to 25 tons capacity was built. The plant

[1] Andrew M. Fairlie, *Chem. and Met. Eng.*, 1921, p. 1006.

consisted of one Glover, five packed cells in series, and two Gay-Lussacs. The packed Glover space was about 15 per cent. of the total packed-cell area, and the packed Gay-Lussac space about 60 per cent. The packed-cell and Gay-Lussacs structures were sheathed with 6-lb. lead. After operating conditions were established, part of the lead sheathing was removed to determine whether acid or gas leakage through the acid-proof masonry was serious. It was found that gas leakage was negligible, and acid leakage was slight. As the acid leakage made the wall wet, a 4-in. veneer wall was laid 2 in. away from the main wall, and tied into the latter at suitable intervals with brick. This, it is said, made a gas-tight wall and a dry, clean outside.

One cub. ft. of gross packed-cell space was provided per lb. of sulphur recovered as acid. In order to produce acid in so small a reaction space it was necessary to greatly increase the concentration of nitrogen oxides in the gas mixture within the reaction spaces provided. Compared with a chamber-system working at the rate of 10 cub. ft. of chamber-space, circulating 25 parts of nitrate of soda per 100 parts of sulphur, the packed-cell process required 70 parts.

The quantity of acid circulated over the Gay-Lussacs amounted to about 300 per cent. of the daily production in terms of 142° Tw.

The advantages claimed for this type of plant are: a saving of 40 to 50 per cent. in first cost, and a saving of 80 per cent. of ground-space.

The South Metropolitan Gas Co. and P. Parish (B. P. 156328) produce sulphuric acid by passing nitrous vitriol through a closed tank, subdivided into compartments by partitions depending from the roof, and immersed at their lower edges in the nitrous vitriol to a depth not exceeding 4 inches. Sulphurous gases are passed through the tank so that they enter one end compartment, then bubble under each partition and leave the other end compartment. There are thus substituted one or more tanks of nitrous vitriol for the known packed absorption towers, and the consumption of power for raising the vitriol is much smaller than is necessary for working towers.

The tank may be fitted with one or more stirrers below the

level of the partitions. Several tanks are arranged in series and worked in the manner usual in conducting reactions between gases and liquids, the gases passing through them either under pressure applied at the inlet, or suction applied at the outlet. With tanks of this kind, the volume of the apparatus may be reduced to 1-1½ cub. ft. per lb. of sulphur converted into sulphuric acid.

Fig. 53 is a longitudinal vertical section, Fig. 54 a cross section, and Fig. 55 a sectional plan of a tank. The tank *a* of suitable acid-proof material is subdivided by transverse partitions *b*, supported on columns *c*, into five compartments each sealed by the nitrous vitriol *d*. The bottom edge of each partition is serrated as indicated in Fig. 54, and the level of the acid is just above the recesses of the serrations.

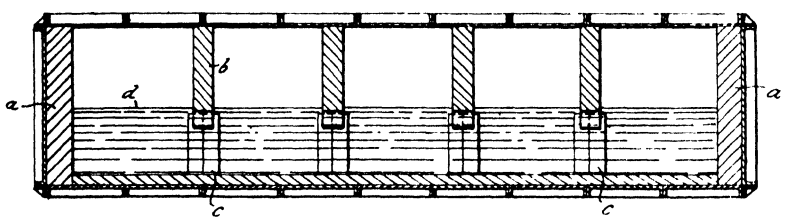


FIG. 53.

The gases containing sulphur dioxide are introduced at one end of the tank at *e* and escape at the other end at *f*, having passed through the surface of the acid in travelling from each compartment to the next by way of the serrations.

The process of K. B. Quinan is described by Wm. Macnab, *Chem. Age*, 1922, vi. p. 872.

The burner-gases are drawn as hot as possible through a Glover tower, where they are cooled to 80°, and at the same time the 66 per cent. acid which is fed to the tower is concentrated to 78-80 per cent. strength.

From the Glover tower the cooled gases and water vapour pass to a bubbler converter, where they are brought into intimate contact with 66 per cent. acid charged with nitrososulphuric acid, the sulphur dioxide being completely converted into sulphuric acid.

The converter consists of a vertical cylinder fitted with a number of diaphragms or plates perforated with a large number

of small holes; overflow pipes projecting the desired height above each diaphragm permit the flow of the acid from plate to plate down the converter.

The gases enter underneath the lowest diaphragm and pass through the small perforations with such velocity that a depth of, say, 1 in. of acid on the plate is kept in violent agitation and

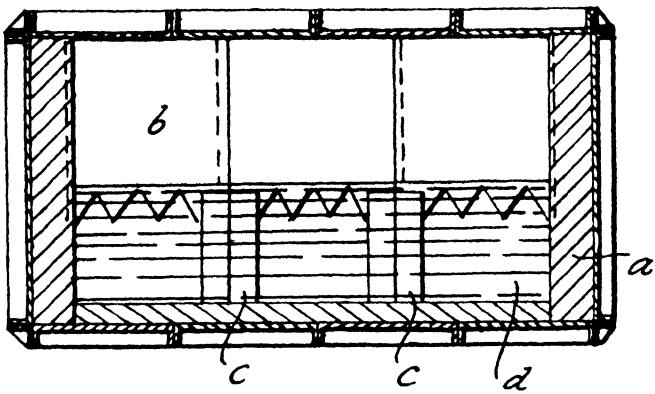


FIG. 54.

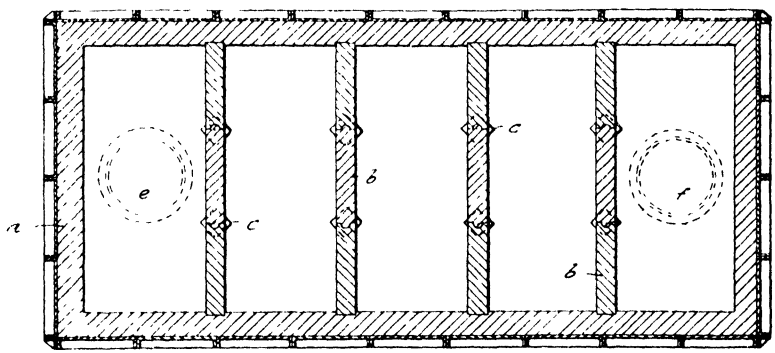


FIG. 55.

prevented from passing down through the perforations. All the gas is thus brought into intimate contact with the descending sulphuric acid on all the diaphragms, with the result that the gas issuing from the top of the converter is free from sulphur dioxide, but charged with oxides of nitrogen.

The heat produced by the formation of sulphuric acid is controlled by the large amount of acid which is passed through the converter, and the process is easily regulated.

Two Gay-Lussacs are used in series, and liquid nitric acid is used to make up the loss of nitre.

The size of a converter for an output of 2 tons of acid per hour of 66 per cent. strength is about 9 ft. diam. by 10 ft. high.

The special requirements of this process, in comparison with the chamber-process, are a more powerful blower to overcome the resistance to the passage of the gases through the converter; more acid to be circulated through the system, and the cooling of the acid as it emerges from the converter; also provision of sufficient acid-storage tanks to compensate for the storage afforded by the chambers themselves.

The Kaltenbach Pipe Process (B. P. 159156 of 1921) is described by A. M. Fairlie,[1] the main characteristics being as follows:—

(1) The dissipation of the evolved heat in the immediate vicinity of its generation.

(2) The possibility of regulating both the reaction temperature and the acid concentration simultaneously to obtain the most favourable conditions.

(3) Intimate contact between the reacting gases and liquids.

The apparatus consists of a great number of pipes or tubes packed inside and water-jacketed outside. The gases from the Glover tower proceed through the tubes of successive systems, in counter-current to the acid, which is mixed as required with appropriate quantities of water. The gases are fed to the parallel tubes comprising any group in a series, through a common header, and devices are provided to assure the regular distribution of acids and gases in the tubes. The dimensions and shape of the tubes have been carefully designed so that the cooling effect of the water-jacket may be felt at the centre as well as the walls. The number of tubes installed depends on the volume of gases to be treated.

The elimination of the heat of reaction by external cooling is claimed to be twenty times as effective as the cooling effect of air-cooled lead-chambers, and this is combined with the practice used in the tower process (see p. 79) of circulating cooled acid through packed spaces, in counter-current to the flow of gases.

[1] *Chem. and Met. Eng.*, 1921, p. 1005.

The advantages claimed are as follows:—

(1) Great ease of controlling the reaction temperature, by means of the circulation of water in the water-jackets, and of cooled acid within the tubes.

(2) Effective utilisation of the surface of the tubes for the exchange of heat.

(3) Ease of isolating one or more tubes for cleaning or repairing, without affecting the rest of the plant.

(4) Reduction in the amount of lead and other materials of construction used, thus reducing first cost.

(5) Possibility of limiting the number of tubes used to precisely what is needed for production required.

(6) Complete independence of atmospheric conditions.

(7) Less difficulty in concentrating the entire production to 142° Tw. by making use of the heat generated in the reaction.

(8) Elimination of water-atomising apparatus.

C. J. Reed (U.S. P. 1363918, 1920) heats a mixture of air, sulphur dioxide, and oxides of nitrogen, and absorbs the products in concentrated acid, subsequently recovering the sulphuric acid by eliminating the oxides of nitrogen.

R. Moritz (B. P. 172009) describes a series of towers which are provided with surfaces capable of withdrawing or supplying heat. This exchange of heat is effected by means of tubes, water from the hottest tubes being used to supply heat to the cooler towers. The towers are preferably of rectangular section, and the acid-proof filling is so designed as to allow the gases to pass through horizontally. The towers are divided into compartments by semi-pervious partitions, which are made of ceramic material and are pierced with small holes, which allow liquids to pass through, but practically no gases, and compel the latter to travel horizontally.

T. Schmiedel and H. Klencke (B. P. 149648) pass the burner-gases through the pipe connected to a small chamber and then to a series of mixers, where they are treated with a large quantity of nitrosyl-sulphuric acid at 119°-134° Tw. in the form of a spray, the unabsorbed gas passing through irrigators. The nitrosyl-sulphuric acid is supplied from a tank to the irrigators, and also to the mixers, the spray being produced by rollers. About 50 per. cent. of the sulphur dioxide is oxidised in a mixer, and oxidation then ceases owing to the

increase in concentration of the sulphuric acid and formation of nitrosyl-sulphuric acid. This acid, together with the nitrous gases liberated in the reaction, is removed by washing in the irrigator. Part of the acid is tapped off from the mixer to the denitrator and removed from the system, the remainder being returned to the tank mentioned above.

Schmiedel's later patent 184966 of 1921 describes a similar process, and mentions that either hot or cold burner-gases can be dealt with. If the gases are hot, the rollers of the mixers may be of cast iron; if cold, of lead or of iron coated with lead.

W. F. Lamoreaux (B. P. No. 198332 of 1922)[1] uses three gas-washers of the Feld type in place of the ordinary chambers. The burner-gas and nitrogen oxides leaving the Glover tower pass through the first washer, in which they come in contact with finely dispersed nitrous vitriol. The mist of sulphur trioxide produced is not condensed there, but passes into the second washer, containing acid of 50° to 61° Bé., which absorbs the nitrous compounds liberated in the first washer. The sulphur trioxide is finally condensed in the third washer, in which 97-99 per cent. acid is circulated. This strength is maintained by the addition of water or steam, or by the addition of weak acid from the Glover.

In cases where fully denitrated acid is not required, the Glover tower is dispensed with.

Instead of the vertical washers mentioned, horizontal Theisen washers may be used.

Opl[2] uses in place of the lead-chambers a series of six closed iron receptacles connected in series, and half filled with nitro-sulphuric acid. Sulphur dioxide is passed through the cylinders, and finally over coke. Acid of 50° to 60° Bé. is produced, and does not attack the iron.

Chamber and Tower Fittings.

Every set of chambers or tower must be provided with a number of fittings which serve to check the process chemically and technically.

[1] U. S. Ps. 1456064-5.

[2] *Chem. Zeit.* 47, 485-6, 1923; *Chem. Abs.*, 17, 2767-8.

Drawing off the acid is rarely done by cocks attached to the chambers direct. These taps soon get stopped up with sulphate of lead, and are not easily repaired when leaking. It is best to place beside the chamber a round or square lead box, open at the top, and of the same height as the upstand of the chamber-bottom (see Fig. 56). The box may be provided with a stopcock, but more usually, as shown in the figure, it carries in its bottom a valve-seat *a*, of regulus metal, into which fits a conical plug of the same metal provided with an iron handle covered with lead.

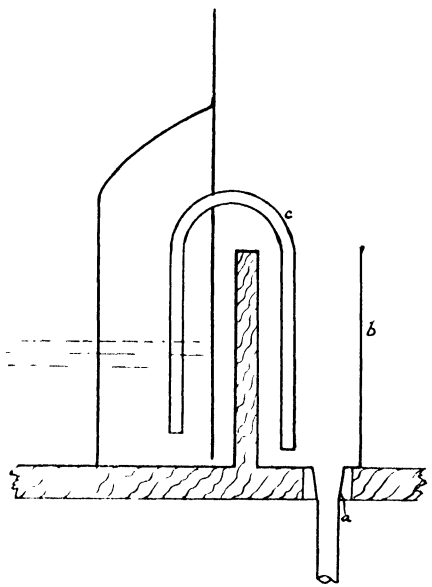


FIG. 56.

Lead siphons *c* are employed for conveying the acid into the box *b*, and these can easily be removed when the flow is to be discontinued.

Another arrangement is shown in Fig. 57. The siphon *b* is firmly attached to the box *c*, or within the upstand of the chamber. A cylinder *d*, surrounding the outer limb of the siphon, is suspended so that it can be drawn up or down by the chain *e* and the pulley *f*, and fixed in any position by the hook *g*. The cylinder *d* forms a continuation of the outer limb of *b*; when it is fully drawn up, so that its overflow *h* is at a higher level than the acid in *c*, it will cease to run; but when *h* gets below this level, the siphon will at once begin to act, all the more quickly the more *d* is lowered. Thus the acid can be run off with more or less speed and with the utmost cleanliness.

Fig. 58 represents a siphon suitable for hot acids in any part of the works. To the top of the siphon *a a* there is joined by a bent tube a closed lead vessel *b*, which is connected with the open vessel *c* by an elastic tube. The latter is filled with

acid and lifted into the dotted position, whereupon *b* and then the siphon *a* are filled; *c* is then lowered, upon which the siphon begins to act, some acid running back from *b* to *c* and thus producing a partial vacuum.

Mention must also be made of the best arrangements for *inserting siphons into glass carboys* or other vessels for carrying corrosive liquids. The simplest and most efficient plan is that shown in Fig. 59. A glass or lead siphon *a* is inserted into a good india-rubber cork, made strongly conical so as to fit bottles with various-sized necks; another short tube *b* passes through the same cork. The siphon *a* may or may not be provided with a tap *c*. It will be seen without further explanation that the siphon can be started by blowing into *b*. The flow of liquid may be stopped either by closing the tap *c*, or, if there is no tap, by lifting out the siphon. In the (very frequent) case where the mouth of the carboy is too irregular in shape for the cork to fit air-tight, the remaining air-channels are stopped up with damp clay, and in an emergency a lump of damp clay may replace the india-rubber cork entirely.

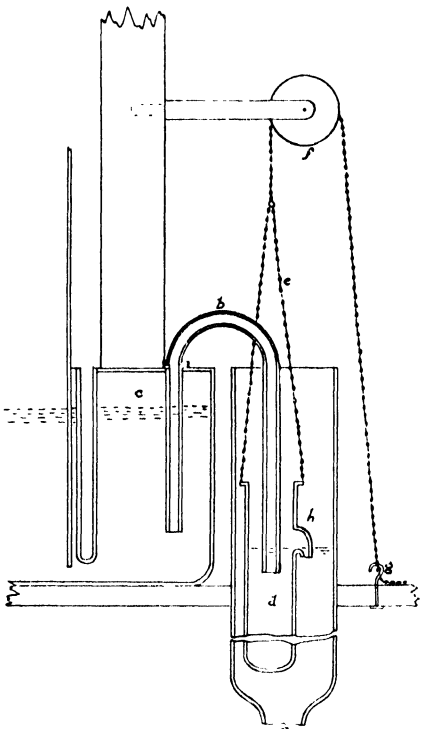


FIG. 57.

Szigeti[1] describes lead siphons for sulphuric acid and aluminium siphons for nitric acid.

Pratt's carboy-emptier, sold by J. J. Griffin & Sons, London, is shown in Fig. 60.

[1] *Chem. Zeit.*, 1915, p. 122.

Acid-dishes (*drips*, *tell-tales*) are placed inside the chambe

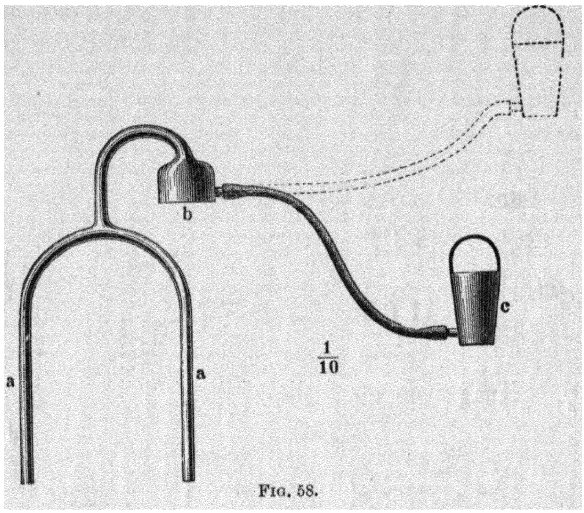


FIG. 58.

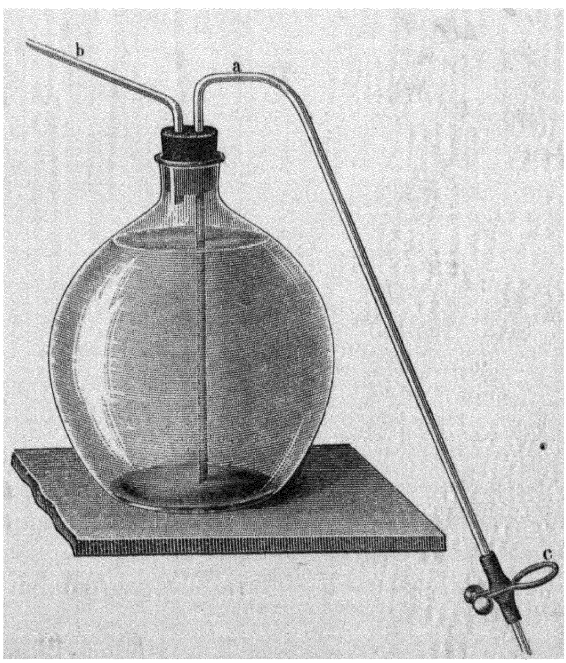


FIG. 59.

in order to examine the process by ascertaining the quant

strength, and nitrosity of the condensing acid. They are made in very different ways. One arrangement consists of a lead vessel, burnt inside against the chamber-side about 3 ft. above the bottom. The acid caught here runs by a tube through the chamber-side into a lead cylinder containing a hydrometer.

Many manufacturers place S-shaped drip-tubes in the connection between the chambers for a similar purpose. Others do not trust to the collectors burnt to the chamber-sides,

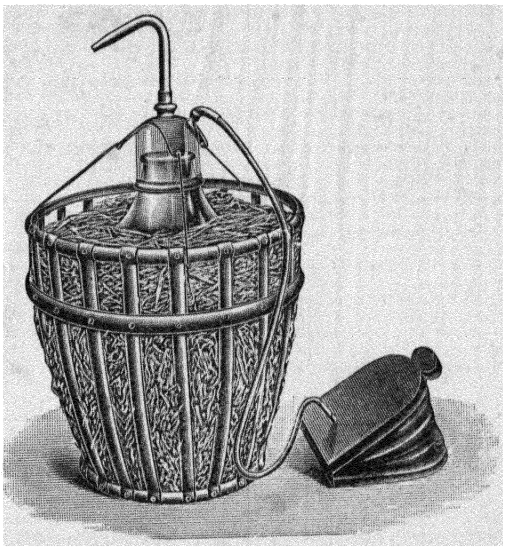


FIG. 60.

but place leaden, glass, or stoneware dishes (A, Fig. 61) at some distance from the side within the chamber. These rest upon a stand of stoneware drain-pipe B, so as to be elevated above the level of the acid; and they have an outlet C, leading outside the chamber. In some works both kinds of drips are fixed side by side. It is noticed that those fixed to the sides always yield acid of 6° to 10° Tw. less than the inner drips, evidently because more aqueous vapour is condensed on the sides along with the sulphuric acid.

The cylinders of acid-drips are generally made very large, but these show the changes in the process much too slowly. It is therefore preferable to make the cylinders very small, holding about 20 c.c., with a side tube and funnel, into which

the fresh drips fall, whilst the cylinder itself keeps overflowing, and thus its contents are renewed about once in every ten minutes (D, Fig. 61). Special small hydrometers, having a range of about 20° Tw., are made for the purpose of showing the strength of acid in these small drips.

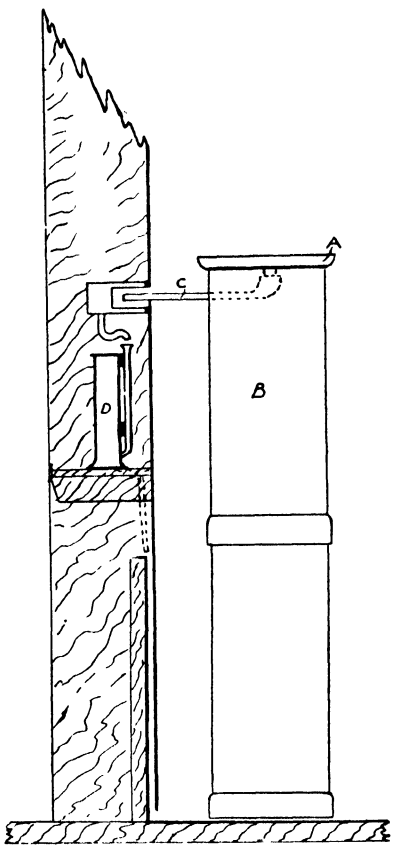


Fig. 61.

For taking samples of the bottom-acid itself, a recess is usually made in some part of the chamber by dressing back the lower part of the side. Some chamber-managers, in order to be quite sure, always take the sample out of the chamber itself through a small hole luted with moist clay; in this case there may be a slight loss of gas, but no danger of getting stagnant acid.

For taking the samples themselves, a dipper of lead or glass is employed, which is lowered slowly, so as to get a sample of all layers of the acid into it. There is often a great difference between the top- and the bottom-acid.

Thermometers are generally fixed at regular intervals in the chamber system, the mercury-vessel of which is inside and the scale outside the chamber. Right-angle thermometers are the most suitable.

For chambers not exceeding 100 ft. in length, one set of drips, thermometers, etc., is generally thought sufficient. For longer chambers this is not the case. At most works there is generally a special set of these fittings for about every 60 ft. length of chamber.

The *pressure* inside the chambers is not easily indicated by the ordinary glass gauges ; the anemometers, however, described at the end of this chapter are quite suitable for the purpose, but hardly necessary for general control of the plant.

Sometimes stoneware plugs are put into holes made in the chamber-sides, in order to indicate the pressure inside the chamber. The tension of the gas is also seen by lifting the covers of the small holes (Fig. 62), which are always placed on the top of the chambers. These covers are fitted into hydraulic lutes, and generally consist of glass jars, so as to give light for observation through the side-windows (see below).

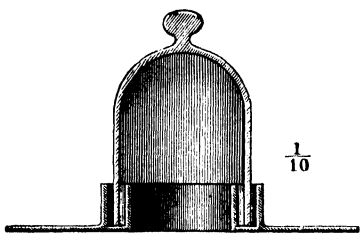


FIG. 62.

For *gauging the height of the acid* in the chambers, either stationary lead gauges (which, however, are difficult to read exactly) or accurately divided copper rods are employed, which are dipped in every time, but always in the same place, since the chambers are never absolutely level.

An instrument for *mechanically calculating the weight of sulphuric acid in the chambers* is described by C. Davidson in *Chem. News*, lxxxvii. p. 205, and *J. Soc. Chem. Ind.*, 1903, p. 625.

Great assistance in judging the chamber-process is afforded by *glass windows* or *sights*, which permit the colour of the gases inside the chambers to be seen. They are 8 or 9 in. square, and are arranged at a convenient height at places in the chamber-side which lie in the same vertical plane as the glass lid covers in the chamber-tops. The chambers are thus sufficiently lighted. Where the chambers are roofed in, light must be procured in some other way (for instance, by two opposite windows in a line with a window in the chamber-shed, etc.). The chamber-glasses are put into small lead rabbets, and luted with white lead and boiled oil. It is sometimes asserted that the colour of the gaseous mixture, observed across the width of the chamber, or in the diagonal line from the side to the manhole-lid in the top, is too deep, and that "sights" in the connecting-tubes are preferable ;

but just the opposite is the case, since the observations are evidently far more accurate and any alterations of colour much more easily perceived in the former than in the latter case. Only in the first part of the chamber is the gaseous mixture, through copious condensation of acid, too opaque for observing its colour; but an observation is not necessary there, as it is only in the back parts of the set that an excess of red vapours is important.

Some works prefer glass jars, similar to those shown in Fig. 62, p. 103, to the ordinary side windows (which are rather difficult to keep clean) placed on special short wide branch-tubes burnt in the sides of the chambers at convenient places. The jars when dirty can be exchanged in a moment for clean ones, and they are supposed to show all the changes in the chamber-atmosphere almost as correctly as the glass panes fixed in the chamber-walls.

Supply of Water to the Chambers.

The water necessary to produce H_2SO_4 and to dilute this to the point required for the practical working of the chambers must be presented to the gases in as fine a state of division as possible. This was formerly in all cases, but is now rarely, effected by injecting into the chamber a certain quantity of *steam*, which rushes forward and on its way is condensed to a mist of very fine particles. At many works, however, water is now injected in the form of a mechanically produced spray.

The Steam

may be generated in an ordinary steam boiler constructed in the usual manner, but made for low pressure, rarely working above two atm., more frequently 1 or 1½ atm. The essential point is to spread the liquid over the whole chamber-space, and low-pressure steam fulfils this requirement, and at the same time sufficiently assists the draught. Low-pressure steam is more easily kept at a uniform tension than high-pressure; and without this, no regulation of the supply of steam to the chambers by the attendant is of any avail. High-pressure steam certainly condenses less readily than

low-pressure steam, but this is a doubtful advantage, so long as the steam possesses enough "carrying-power" to convey the minute globules of water right to the other end of the chamber. Experience has shown that this is the case even with low-pressure steam. At many English works only a single jet at one end of each chamber is employed, and this is considered quite sufficient to supply the whole chamber with moisture (see *infra*).

Of course, low-pressure steam may be obtained from a boiler working at high pressure by means of a reducing-valve. The same boiler may be utilised for driving the machinery of stone-breakers, air-compressors, and so forth.

The chambers may also, of course, be fed with the exhaust-steam of engines, if these are worked so as to leave some pressure in the exhaust. The utilisation of the waste steam of the air-compressor for this purpose had been practised by Lunge for many years, as described in the first edition of his work (1879), vol. i. pp. 393 and 565. A proposal not essentially differing from this was patented much later by Sprengel (B. P. 10798 of 1886, U.S. P. 357107).

The Soc. Anon. Ing. L. Vogel (B. P. 17794 of 1904) procures part of the steam for the chambers by taking away a portion of the burner-gas before it enters the Glover tower, and passing it through a tower packed with stoneware rings or the like, which is fed with water or dilute sulphuric acid, whereby steam is produced and then sent into the chambers.

At some large works, in order to control the uniform tension of the steam, so important for the regularity of the chamber-process, *registering steam-gauges* are employed. A gauge of this type is made by The Budenberg Gauge Co., Ltd., Broadheath.

The *conveyance of the steam* to the chambers usually takes place in iron pipes, with one or more branches for each chamber. Considering their great length, the main pipes should always be surrounded by non-conductors of heat in order to restrict radiation as much as possible, and to avoid a considerable loss by condensation of water. The branch pipes should be treated similarly, if possible.

The pipes are preferably laid with a slight fall towards the boiler, so that the condensed water may run back. Where, from

local circumstances, this cannot be done, apparatus for removing the water should be fixed at the lowest point of entrance to the chamber.

Fig. 63 represents a simple form of trap, the body of which is made from 14 lb. sheet lead and the connections made with the chamber and steam supply as shown.

The condensed water is removed by the drain-pipe as formed, the steam thus entering the chamber in a suitable condition.

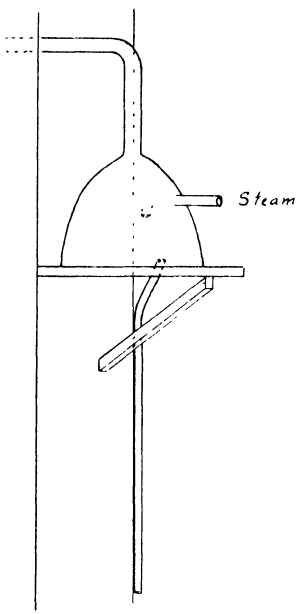


FIG. 63.

Of course, the size of the steam main must correspond to the number and size of the chambers. The *branches* for each chamber need not be above 1 in. diam. even for large chambers (up to 70,000 cub. ft.) supplied by one jet. They are made of wrought-iron tubes *a* (Fig. 64), sometimes of copper, up to a short distance from the chamber, where they end in a cock or valve *b*, to which a lead pipe *c*, equal in bore to *a*, is attached and projects into the chamber itself. It is not, however, burnt to the chamber-side *e*. A short wider tube *d* is burnt to this, and *c* is loosely put into it, the joint being made tight with tar-cement, etc.

The same cut shows another commendable contrivance, viz., a simple mercurial *pressure-gauge*, consisting of a bent glass tube *f*, with a scale *g*, connected with a branch *h* of the lead pipe *c*. Thus the pressure *behind* the regulating-cock can be observed at any time, and the chamber-manager has a means of very accurately regulating the supply of steam. Any water condensed in the gauge can be easily allowed for.

A good *steam-cock* is preferable to a wheel-valve, because the wheel does not show how far the valve is opened, whilst the handle of the cock can be fitted with a graduated arc so that its position can be fixed with precision.

Automatic steam-regulators, if reliable, save a great deal of

trouble, but do not dispense with constant supervision on the part of the attendant, as they are somewhat liable to get out of order.

In England it is usual to employ only one jet of steam for each chamber, either beside, above, below, or even within the pipe conveying the gas from the burners, the Glover tower, or the preceding chamber. Some introduce the steam quite near the top, others in the centre of the chamber-end. A single steam-jet suffices, if the length of the chamber does not exceed about 100 ft.; in longer chambers it would not carry right through.

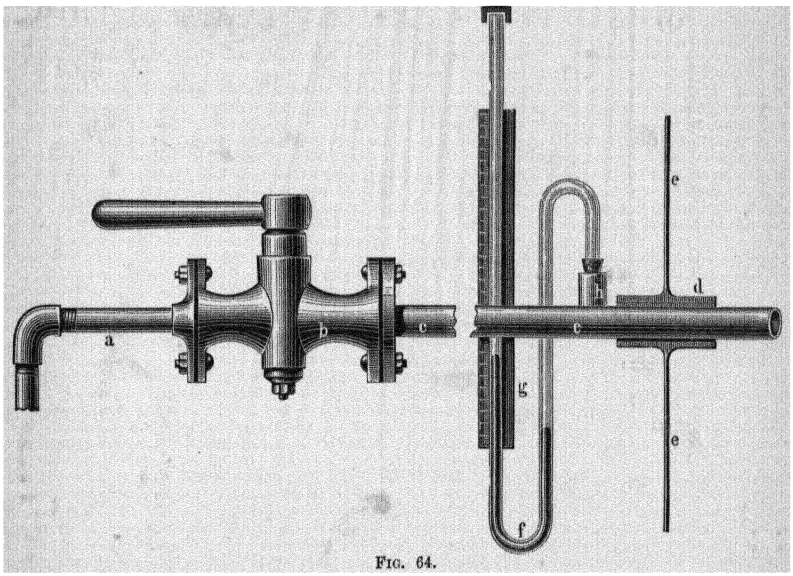


FIG. 64.

It is maintained by some practical men that a single steam-jet from a 1-in. pipe is quite sufficient for feeding chambers up to 130 ft. length, and also that the distribution of moisture through the chambers is thus properly effected. It is preferable that the steam-jet should enter the chamber near the top, or at least in the upper part of the side. Experience has shown that it is not advisable to send the steam into the lower part of the chamber.

Most experienced managers, however, now agree that the single steam-jet for each chamber is a faulty appliance. The chamber should not be left to haphazard supply of its different parts with the necessary amount of moisture, but each part should receive just what it needs.

On the Continent, indeed, most manufacturers have always preferred employing a number of steam-jets for each chamber, so as to make themselves independent of any casualties in the proper distribution of steam by a single jet. These branch jets are introduced at right angles to the direction of the gaseous current either in the long chamber-sides, not far from the top, or, as is most usual, through the roof of the chamber, so that the single jets can be regulated by a man walking over the top.

Where a Glover tower is in use, the first steam-jet should not be in front of the first or "leading" chamber, as this part receives enough steam from the Glover tower. The first steam-jet should be 20 or 30 ft., or even farther, from the front side.

The total quantity of steam required for a set of chambers, which should be known approximately in order to fix upon the boiler-space and the size of the main pipes, depends, of course, firstly upon the quantity of sulphur to be burnt, secondly upon the existence of a Glover tower, and thirdly upon the strength to which the acid is brought in the chambers. A general rule, therefore, cannot be laid down. The two latter conditions are partly reciprocal; the stronger the acid is made in the chambers, the less water is evaporated in the Glover tower, and *vice versâ*. If it is assumed, adopting a proportion very usual in England, that all the chamber-acid is brought up to 124° Tw., and that it is concentrated in the Glover tower up to 148° Tw., the amount of steam required will be as follows:—

Every pound of sulphur burnt requires,

1st, for forming $\frac{98}{32}$ SO_4H_2, $\frac{18}{32}$ water .	= 0·5625 lb.
2nd, for diluting it down to 124° Tw. (= 70 per cent. SO_4H_2), $\frac{30 \times 98}{70 \times 32}$.	= 1·3125 ,,
	1·8750 ,,

Of this nothing is lost with the escaping gas, as this passes in the Gay-Lussac tower through strong vitriol. The Glover tower saves the steam corresponding to a concentration from

124° (= 70 per cent.) to 148° Tw. (= 80 per cent.), viz., $\frac{10 \times 98}{70 \times 32}$ . .	= 0·4375 ,,
Leaving . . .	1·4375 lb.

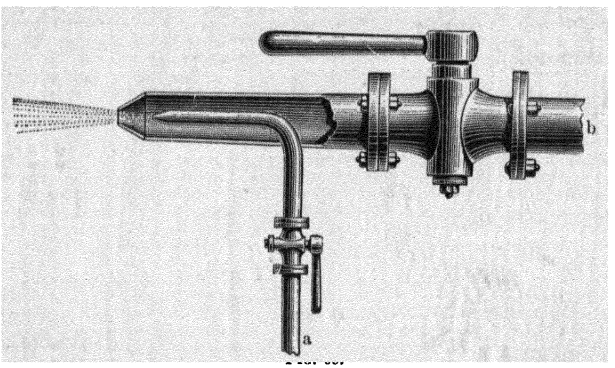
which must be supplied to the chambers. To this must be added a certain quantity for water condensing in the steam-pipes. This amount cannot be estimated generally, since here everything depends upon the length of the pipes, their thickness, surroundings, etc. On the Continent, the chamber-acid is kept more dilute and correspondingly more steam is used. It is safe to say that the steam to be generated in the boiler, without a Glover tower, amounts to about two and a half times the weight of sulphur burnt; and with a Glover tower, to about twice the weight of sulphur burnt.

Introduction of Water in the form of Spray.

Instead of feeding the chambers with steam, Sprengel (B. P. of 1st October 1873; U.S. P. 150095 of 1874) proposed to employ liquid water in the form of a fine spray. His reasons are, that the steam increases the volume of the gases by its heat, and consequently more chamber-space and nitre are required, which can be avoided by introducing the water in a liquid form, sufficiently divided; and that the cost of evaporation can be saved in this way. The water is made into a spray by the employment of steam, a steam-jet of 30 lb. tension escaping through a platinum nozzle in the centre of a water-jet, as shown in Fig. 65 (where *a* is the steam-pipe, *b* the water-pipe); 20 lb. of steam is sufficient for converting 80 lb. of water into a mist. These jets are arranged in the chamber-sides, at distances of 40 ft. apart, and supplied with water from a tank fixed at some height above. Of course, the water- and steam-cocks must be accurately regulated, and the two nozzles must have a particular shape, so that only a fine mist is formed. If larger drops were formed, they would at once fall to the bottom and dilute the chamber-acid.

A different way of producing a spray or mist of water instead of a steam-jet for feeding vitriol-chambers has been introduced with great success into several factories. The spray is produced by allowing the water to issue at a pressure of several atms. from a small platinum jet against a small platinum disc. These water-jets are introduced in the chamber-top, at distances of about 10 ft. Thus the whole

chamber is uniformly filled with a fine mist, which, together with the steam coming from the Glover tower, supplies all the water required for the chamber-process. The water must be carefully filtered, as otherwise the jets would soon be stopped up; but this trouble is far more than compensated by the considerable saving in fuel caused by doing away with the steam-boilers. The fear formerly entertained, that the introduction of the moisture in the shape of liquid water would reduce the temperature of the chambers below that most favourable for the acid-making process, is entirely groundless.



The point might be raised that steam is preferable on account of being only gradually condensed in its onward course within the chamber, and that the moisture would thus be more uniformly distributed through the chamber. This objection is, however, not valid, and would not be so even if no sulphuric acid were present in the chamber. Calculation shows that, for each kilogram of sulphur, the gas introduced, whose volume at 50° and 760 mm. pressure amounts to 8345 l., can contain only 0·6868 kg. of aqueous vapour, whilst the total amount of water is nearly four times as much, and three-fourths of the steam entering into the chamber must therefore be at once condensed into water. This calculation, given in Lunge's first edition, pp. 348 and 349, does not take into account the fact that the tension of aqueous vapour within the chamber is very much reduced by the presence of sulphuric acid, and is hence useless for this purpose. Hurter[1] more

[1] *J. Soc. Chem. Ind.*, 1882, p. 51.

correctly applies Regnault's table for the tension of aqueous vapour in sulphuric acid of various strengths, and gives a diagram which allows this tension to be found for any intermediate concentration of acid. Hurter's values, however, are not applicable to the principal working part of the vitriol-chamber, as Regnault's determinations go only as far as 35°—that is, much below the ordinary chamber-temperature—and it is not admissible to calculate tensions at 60°, 80°, or higher by simply applying Regnault's table or Hurter's diagram to them. This gap has been filled by a set of elaborate observations made by Sorel, and first published by Lunge.[1] Sorel's table extends to acids from 44 to 82 per cent. H_2SO_4, and to temperatures from 10° to 95°. It is given in Chapter III of Vol. I, p. 215, where the specific gravities corresponding to the acid percentages have been added for the reader's convenience. At the close of this chapter a table is given for reducing volumes of gases to the conditions of the vitriol-chamber atmosphere, which also takes into account the aqueous-vapour tensions of sulphuric acids of various strengths.

The importance of this table will be indicated at present by only one example. In a special instance, the temperature close to the chamber-side was 80°; the acid running down the side stood at 114° Tw. = 66 per cent. H_2SO_4, and the aqueous-vapour tension at this place was, therefore, 39 mm. Only 6 cm. (say 2½ in.) within the chamber the temperature was 95°; but at this temperature an acid, the aqueous-vapour tension of which is 39 mm., must have a strength of 128½° Tw. = 72·33 per cent. H_2SO_4, and this was found to be really the case. The importance of this is shown in Chapter III.

Looking at the great reduction of the tension of aqueous-vapour by the presence of sulphuric acid, we must conclude that the steam introduced into the chamber is condensed almost immediately into a liquid mist, and this must reduce to almost *nil* the alleged superiority of the "carrying power" of steam to that of a properly comminuted spray of water, introduced at high pressure.

Of course, the water *must* be properly comminuted; otherwise, when it drops from the jets in the shape of rain, it dilutes the chamber-acid to an intolerable degree. This is all the

[1] *Z. angew. Chem.*, 1889, p. 272.

more injurious as the dilute acid floats on the top of the stronger chamber-acid, and is not noticed at the places where the acid is drawn off, until it is too late to remedy the evil. This accident will happen whenever the jets are out of order, and has caused several works to abandon the plan of introducing the water in the shape of a liquid spray.

A special jet for converting water or acid liquids into a fine spray is supplied by Benker & Millberg, of Asnières, near Paris, and is shown in Fig. 66. It is constructed to deliver from 2·2 to 7·7 gallons per hour, and is made with either plate or screw.

In order to harden the platinum from which the jets were originally made, Benker & Millberg now add about 10 per cent. of iridium, and this prevents the size of the outlet enlarging,

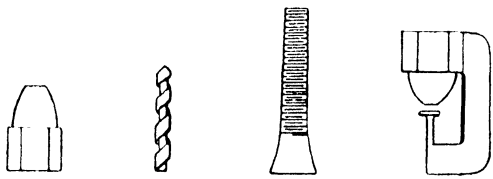


FIG. 66.

as occurs in those made of pure platinum or gold. Considerably over 30,000 jets have already been supplied.

For all types of spray-producers the water must be carefully filtered, preferably by means of sponge filters. Benker & Millberg's arrangement of the apparatus necessary is shown by Fig. 67. A is a large filter filled with sponges; B, the water reservoir, the necessary head of water being maintained by the ball-valve H; C, the centrifugal pump for maintaining the necessary pressure; D, small sponge filters; and E, the water spray-nozzle in the chamber-top.

In case of breakdown of the pump, town's-water may be applied by the connection F, and an overflow pipe G is provided in order to drain the pipes.

Scherfenberg and Prager (Ger. P. 219789) supply the water required for the chamber-process by spraying it upon undulated, perforated surfaces inside the chamber. Before the water arrives at the bottom, it is converted into sulphuric acid. By this means the chamber-space is much better utilised, as in reaction-towers. In the cooler back part of the chambers steam may be used instead of water, as here it condenses at

once, and the higher temperature thus produced is useful. Instead of water, dilute acid may be used for this purpose.

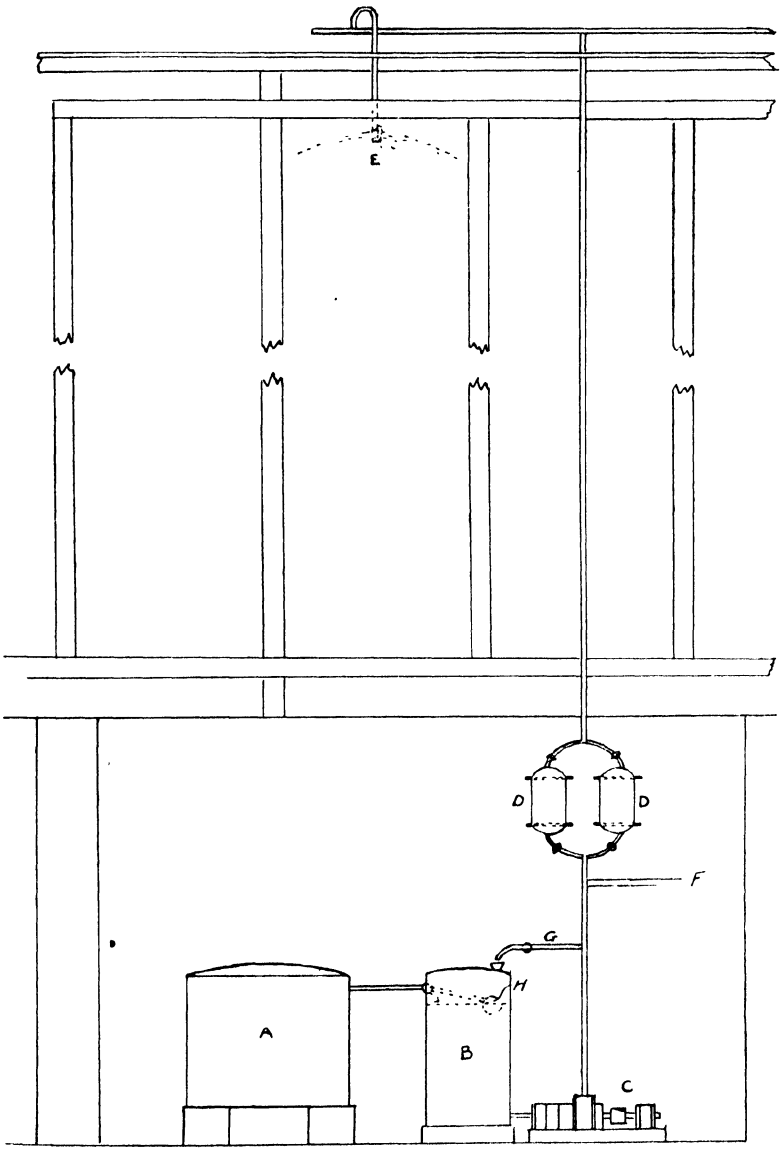


FIG. 67.

Rabe (Ger. Ps. 237561 and 246240) describes a controlling

apparatus for spray-producers in the chambers, consisting of a glass tube placed in a suitable part of the entrance-pipe. In this tube is a glass ball, which takes a higher or lower position according to the quantities of water flowing through the tube. A tap in the same place admits of regulating the corresponding tuyere. In this way the whole of the spray-producers of a set of chambers may be regulated from a single point, without checking each individual spray.

Gaillard (B. P. 11732 of 1908; U.S. P. 909578) describes an arrangement of conical extensions in the roof of the chamber to increase the height of the nozzle of the spray-producer. A tray is placed underneath to catch the coarser drops, and the water so caught is conveyed away from the chamber to prevent its diluting the chamber-acids.

Santa (B. P. 18615, 1913; Ger. P. 273665; Fr. P. 461741) describes an apparatus for the automatic regulation of the concentration of the acid made in the chambers by automatic regulation of the work of the spray-producers. It consists of a balance, into which acid flows from the chamber-walls. If the density of the acid is above or below the normal, the balance goes out of level and starts a lever by which a valve in the water-conduits is correspondingly set. One form of this apparatus consists of a lever, with a counter-weight, on which is suspended a cup taking up the acid, fitted with an overflow started from the bottom of the cup. In another form, the lever of the balance is provided with projections which in turn start two levers by which the water-valve is worked by means of an eccentric. The specification also describes other forms of the apparatus.

Schüphaus[1] discusses the advantages of supplying the acid-chambers with water-sprays, and states that the water is best preheated to 60° to 70°.

Haughton's Metallic Packing Co., London, sell an acid-spray-producer of new shape for application in vitriol-chambers, in connection with a centrifugal pump made of acid-proof material. This sprayer is easily and cheaply applied to existing chambers.

Sache employs spray-producers with glass points. The middle part is made of lead, and the supply-pipe of bronze.

[1] *Metall und Erz*, 1915, p. 504; *Z. angew. Chem.*, 1916, 2, 171.

W. Szigeti[1] describes a sprayer in which water at 60-75 lb. pressure passes through a plate by three holes and then along three grooves, whence it passes tangentially into a small chamber, one side of which is a tantalum plate pierced at the centre; the water emerges through the perforation in a fine spray. The body of the apparatus is of hard lead. The tantalum, owing to its chemical indifference to acid gases combined with mechanical strength, can replace platinum with advantage.

Körting Brothers' spray-producer (Fig. 68) contains, within the contracted part, a metal spiral, which by the pressure of

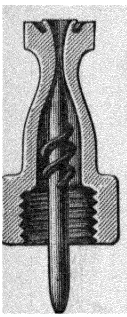


FIG. 68.

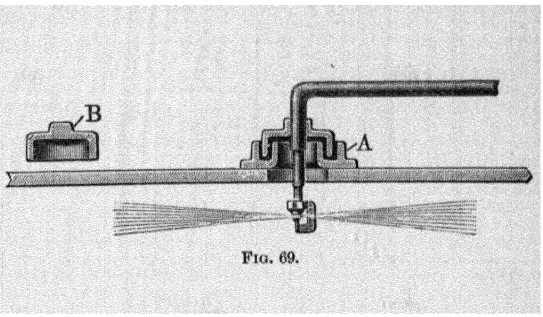


FIG. 69.

the liquid is kept tightly in its place, whilst the liquid on passing through the helical channel takes a rotating movement, so that on issuing it is projected equally on all sides as a conical spray. The nozzle and spiral spring can be arranged for sprays of any degree of fineness. This apparatus was originally intended for damping the air in cotton-mills, etc., for precipitating dust, for absorbing acid vapours, and so forth. It has also been made of platinum, and is in several places used for producing a fine spray of water in vitriol-chambers.

These Körting spray-producers ("Streudüsen") were also made of antimony-lead with a platinum lining, but this did not stand the corrosion in acid-chambers, and had to be replaced by solid platinum nozzles.

Fig. 69 shows another type of spray-producers also made by Körting Brothers. They produce a flat, horizontal spray, and are made of glass. They are placed in the hydraulic seal A, which is closed by the cover B, and are put in their places

[1] *Chem. Zeit.*, 1918, 42, 115.

only when the chamber is at work. They are left in action whilst taken out for examination, and are joined to the water-main by lead or flexible piping. In order to prevent their being stopped up, each nozzle is protected by means of a separate strainer, in addition to a larger main filter upon the ground-level.

The following table gives their sizes and capacities:

Size.	Diameter of orifice in m/m.	Gallons of water atomised per hour, at 60 lb. pressure.
S	$\frac{1}{4}$	1·45
,,	$\frac{5}{8}$	1·85
,,	$\frac{3}{4}$	4·
,,	1	8·
,,	$1\frac{1}{2}$	14·
L	2	25·
,,	$2\frac{1}{2}$	40·
,,	$3\frac{1}{2}$	58·

The Monarch Manufacturing Works, Inc., Philadelphia,[1] are now selling their new "Perfection" stoneware chamber-spray (Figs. 69*a* and 69*b*), which is considerably more efficient than their heretofore well-known "Improved" type. Their operation (assuming reasonably clean water) is absolutely positive at all times, without streaks or drops and without variation in capacity, particularly increase. This is possible because of the fact that the two parts of the nozzle, tip and disc, having to do with the atomisation are both made of stoneware, and the wear of orifice over a long period is comparatively little.

These Monarch "Perfection" chamber-sprays fit all existing lead parts heretofore supplied, although additional sizes have been added, so that the acid-maker is now able to select exactly what is required. For instance, they are furnished with different-size orifices to deliver, at 60 lb. pressure, 2·5, 4·3, 4·9, 7·5, 12, 14, 18, and 23·6 U.S. gallons per hour; while in the No. 2 size they are furnished to deliver, at 60 lb. pressure, 17·5, 28, 38·5, 41·7, 46·0, 55, 69, and 75 gallons. Special nozzles are also made delivering as much as 300 gallons per hour.

A spray-producer, made of glass, and sold by the name of

[1] Agent, H. T. Watson, 46 Fairfield Road, Widnes.

"Skorpion," is recommended as being very simply constructed and producing a hardly visible veil of water, without the formation of drops. It is worked at from 3 to 8 atm. pressure.

Poley's spray-producer is protected in Germany by D. R. G. M. 3139, and is shown in Fig. 70. For acid-chambers it is always made of glass. The tube, introduced into the chamber-wall by a rubber stopper, has a conically shaped end inside; the liquid is caused to assume a whirling motion by the glass or hard-lead spiral placed in the contracted part. The junction with the water-conduit is made by an ebonite screw, with rubber rings inside. This apparatus sprays at a pressure of 4 atm. in the water-conduit from 20 to 24 litres of water per hour. Other details are given in the text. The removal of this apparatus for control is much easier than in the case of platinum spray-producers.

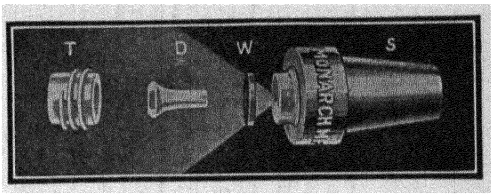


FIG. 69a.

The Harkortsche Bergwerke und Chemische Fabriken (Ger. P. 275388) convert the water into spray by a glass vessel, provided with a central outlet opening, and with grooves running from the top downwards in curved paths; a glass ball partially closes these grooves. The outside parts are made of hardened lead, the glass parts of a special glass mixture, resisting great changes of temperature. Fig. 71 shows this apparatus. If the top part *a* is connected with the water-conduit and the tap is opened, the water rushes under pressure into the lower part *b*, and presses the ball *i* upon the glass vessel *k*. The water forces itself through the grooves, gets into the fine bore *l*, and leaves this in the form of a spray. When the grooves of the vessel *k* are getting stopped up, the pressure of the ball *i* is loosened,

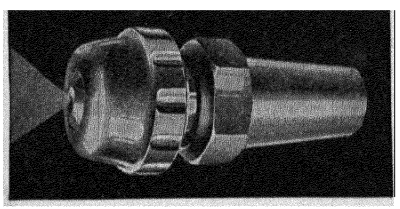


FIG. 69b.

whereupon *i* rises and the water-particles are thrown out as a full jet.

A. Primavesi, of Magdeburg,[1] supplies low-pressure spray-producers with an ebonite nozzle.

The only drawback to the spray system is the liability of the orifice of the spray-producer to get choked up by dirt, or

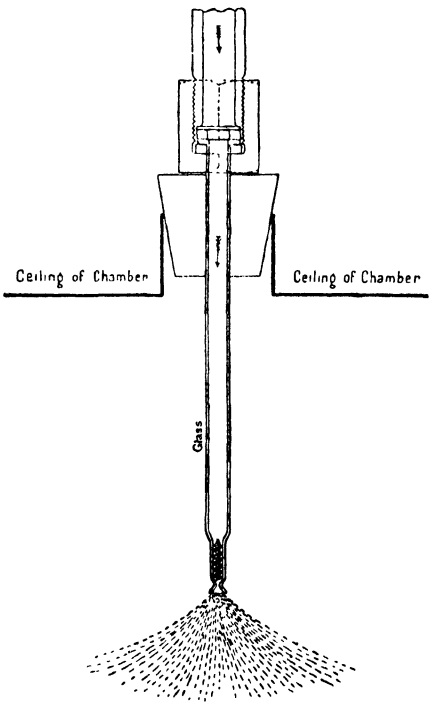


FIG. 70.

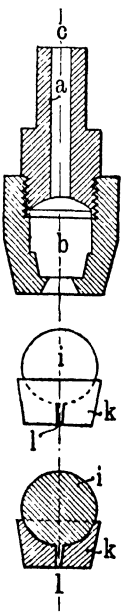


FIG. 71.

else to be widened by corrosion. The former is avoided by careful filtration of the water, the latter by a suitable construction. Glass nozzles, as shown above, are much better even than platinum. Lunge found this system applied for many years with full success in a number of the best-managed works, *e.g.* Griesheim and Aussig. Wherever it has proved unsuitable, the cause has been lack of attention.

Benker and Hartmann[2] make the following calculation.

[1] *Chem. Zeit.*, 30, 300.

[2] *Z. angew. Chem.*, 1903, p. 864; *J. Soc. Chem. Ind.*, 1903, p. 344.

According to Lunge's calculations, the conversion of each gram molecule of SO_2 (64 grams) into $H_2SO_4,3H_2O$ (which is the approximate composition of chamber-acid) liberates 65,500 calories. These 64 grams SO_2 require, for their conversion into sulphuric acid of the above strength, 72 grams water. Each gram of steam, introduced into the chamber (at 60°) with a temperature of 120°, yields 606·5 (0·305 × 120) − 60 = 583 cal. Hence the total heat evolved is: 65500 + 583 × 72 = 107,476 cal. If, however, the water is introduced in the liquid state at 15°, it must be heated up to 60°, and that amount, 72 × 45 = 3240 cal., must be deducted from the 65,500 cal., leaving but 62,260 cal., or a difference of 45,216 cal. as compared with the use of steam.

Nagel[1] discusses the introduction of water in the form of spray into vitriol-chambers. Care should be taken that all the gas for the chambers is forced through the tuyeres as well; this is attained by connecting the pipe leading from the Glover tower into the first chamber, with the entrance opening off the steam spray-producer. The bottom part of the casing for the blast should be made wider than all other parts, and here the gas should be cooled down to 65° by a tubular air- or water-cooler. The gases should go from the Glover tower through the spray-producer into a small chamber, and from this through two reaction-towers into the Gay-Lussac tower. The gas enters the apparatus preferably at atmospheric pressure, so that the blast acts only as a mixing agent. In this way 20 cub. m. air may be aspirated by 1 kg. steam of 2 atm. pressure.

Norton[2] reports from personal observation that at the factory of the "Union" at Kratzwieck, near Stettin, where water-spray-producers are employed, they work at a chamber-space of 10½ cub. ft. per lb. sulphur per 24 hours, with a consumption of about 0·5 kg. nitric acid 36° Bé. per 100 kg. chamber-acid, whilst formerly 0·7 to 0·8 kg. nitric acid was required. The "Union" feeds its chambers only during the warm season with water-spray, but in the winter time with steam.

Other forms of spray-producers for vitriol-chambers are described by Düron (Ger. P. 221779); General Chemical Co.

[1] *J. Soc. Chem. Ind.*, 1914, p. 522.
[2] *J. Ind. Eng. Chem.*, 1912, p. 534.

(U.S. P. 1032657); Parent (Fr. P. 462349); D. H. Thomas (B. P. 19867 of 1912).

In the *57th Alkali Report* (1920), p. 15, the following remark occurs: "Water-sprays are in use in place of steam, the height of the chambers being at the same time considerably increased by reason of the adoption of the water-sprays. The resulting intensive work has brought down the chamber-space in many cases to 8 cub. ft. per lb. of sulphur per 24 hours."

Dilute sulphuric acid, e.g. from the last chamber, instead of pure water, is used for the introduction into the chambers by spray-producers by several inventors, *e.g.* Guttmann (B. P. 18927 of 1906), Rabe,[1] Scherfenberg and Prager,[2] etc.

Delplace (Fr. P. 342117) washes cooled burner-gases with strong sulphuric acid, in order to take out any SO_3 present, compresses them, and then applies them to injectors by which the water for the chambers is converted into a spray.

Foster (U.S. P. 1277896) subjects the chamber-gases to the action of atomised chamber-acid, which is injected by means of air-blasts and in the direction of the gas-flow at a number of points along the connecting flues.

Production of the Draught in Acid-chambers.

The draught necessary for working acid-chambers is produced by various agencies, the most important being the high temperature with which the gases leave the burners and enter the chambers, which counterbalances the greater density of the burner-gases when compared with that of air in the cold state.

Lunge, in his fourth edition, p. 738 *et seq.*, gives the calculations for the density of the burner-gas compared with cold air, and also deals with the draught produced by the formation of sulphuric acid in the process. He also compares the gases from the burning of sulphur with those from pyrites, and discusses the regulation of the air entering the burners.

The volume of air necessary for a certain consumption of sulphur is, of course, also dependent upon the elevation of the site above sea-level, which regulates the mean barometric

[1] *Z. angew. Chem.*, 1910, pp. 8 to 12.
[2] *Supra*, p. 112.

pressure. Thus at Munich a quantity of air will occupy a space larger by 5·5 per cent. than the same quantity at Widnes or New York.

It is easy to introduce the minimum of air required for proper work. An excess of air is, like a deficiency, injurious, although not to the same extent. Air in excess cools the gas, and thus may sometimes interfere with the process; it fills a portion of the chamber-space by diluting the gases, thus weakening the energy of the chemical action. The regulation of the supply of air must therefore be accurate, and must be adapted to the frequent variations in the state of the atmosphere. This must be done by regulating the openings for introducing the air, or for taking away the exit gases, according to the state of the chambers. For instance, if the chimney-draught is too much cut off, the gas issues forcibly from any openings in the chambers, etc., whilst the air may enter properly by the holes in the front of the burners. If, however, these latter are closed too much, the chambers suck in air in any places not completely closed against the atmosphere.

The draught may also be increased in two different ways, viz., by enlarging the opening in the exit-tube, or by increasing the inlet-holes in the door of the burner. Then the chambers, if the exit-tube is not sufficiently closed, suck in air; if, on the other hand, the inlet-openings are too wide, gas is forced out from any leaks in the chambers by the excess pressure. This is especially noticed when the doors are opened for charging. Both faults can be avoided by arranging a certain proportion between the inlet and the outlet openings. Usually the area of the latter is two-thirds that of the former. No certain rules can be given for the changes of draught made necessary by the variations in the state of the atmosphere; observation and practice must come into play here. In well-arranged works, however, this is not left to chance, but the supply of air is checked by regularly estimating the oxygen in the escaping gas, as will be seen later on.

The hot gaseous mixture in itself contains the conditions for causing a draught, since it is much lighter than the air, and will always have a tendency to rise from the burners to the chambers. The second source of draught, viz., the formation of liquid sulphuric acid within the chambers from the mixture

of the gases, must also have an aspirating action, not only from the burners, but from all sides.

Together with these two sources of draught furnished by the peculiar nature of the acid-making process itself, there must always be another arrangement for causing further draught, otherwise the current of gas could not be turned into the required direction. In the simplest case, a plain *outlet-pipe* behind or above the last chamber or Gay-Lussac will suffice. The Belgian Commission of 1854 even preferred this arrangement to a chimney, because the latter might produce an excessive draught. This objection, however, is obviously not important, for it is a very easy matter to cut off an excess of draught by a damper, etc., in the outlet. On the other hand, it is much more difficult to increase the draught in the outlet pipe or chimney, if insufficient. For the latter object, a steam-injector placed in the outlet-pipe was formerly considered the most convenient apparatus. Sometimes, instead of a proper injector, a simple steam-jet, turned in the direction of the draught, is employed; but this is a very wasteful proceeding, and a proper Körting's injector, made of regulus metal (lead and antimony), should always be employed.

Steam-injectors between the Glover tower and the chambers are impracticable. This holds good of any place in the system, except in the exit pipe or chimney itself; but if placed in the chimney, where the steam cannot be utilised for the chamber-process, they cause considerable expense.

Chimneys.—It must not be overlooked that, in the case of employing steam-injectors, good regulation is all the more called for, lest the draught should be too strong; and in the end a cheap source of draught, viz., a chimney, has been replaced by an apparatus requiring much supervision and regulation, and which is, moreover, costly to work. Accordingly, in ordinary cases a chimney is preferable to a steam-jet, as the former will be necessary in case of a steam-boiler being required on the works. Of course, the chimney, to do its work, must be higher than the chambers.

Where a chimney cannot be employed, for any reason, nothing remains but to have recourse to a fan.

It answers much the same purpose as a chimney if the outlet-pipe fixed to the last chamber has a considerable height

—for instance, 50 ft. (as is the case in the south of France). Where several sets of chambers exist in the same works, it is preferable to carry them all into a common chimney, providing the connecting-pipe of each set with a contrivance for regulating the draught. It is not a good plan to utilise for the chambers a chimney with which ordinary furnaces are connected, as the draught will be of a very variable character in this case, and the working of the chambers will not be easily kept regular. Still, at some works this plan cannot be avoided, and must be provided for by more careful regulation of the draught. For such works more than anywhere else, the automatically acting dampers, described below, are recommended.

The employment of a chimney is even more advisable if, as is now the case in all well-appointed works, a Gay-Lussac tower is placed at the end of the set. In this case, the draught must be regulated with even greater care; but there must be an excess of draught at disposal to begin with. It is also a great improvement if the "sight" necessary for checking the work of the tower (*cf.* Chapter II) can be arranged in the down-draught near the ground-level, or at least the gangway round the chambers. If there is no down-draught, but a direct top-draught out of the tower, it is always necessary to mount to the top to observe the "sight." It is certainly quite possible to employ the tower itself as a chimney, if it is built with its top a good deal higher than the chambers; and this is actually done at a good many works, but probably in some cases only because there is no chimney available.

Very frequently one chimney has to serve two or more sets of chambers. It is perfectly well understood, from innumerable analogous cases in ordinary firing operations, that, where several pieces of apparatus are served by the same chimney, special care must be taken that they receive the same amount of draught. Wherever possible, the main flues are taken separately to the chimney and are introduced into the latter in such a way as not to interfere one with another, which can be attained by erecting mid-feathers within the chimney. Where it is necessary to connect several sets of chambers with the same main flue, it must not be overlooked that the draught is stronger in the part nearer than in the part farther removed from the chimney; by suitable arrangement of the dimensions, by

avoiding sharp angles in the places where the branches form the main flue, by mid-feathers, and by regulation by means of dampers, a proper equalisation can generally be attained.

Other Arrangements.—Sometimes none of the ordinary measures secure an equal draught for two sets of chambers, even when the flues from these meet about the same distance from the chimney. In these cases it is best to make the individual flues end in a large chamber, from which the main flue leading to the chimney starts, and to fill this chamber loosely with bricks, but not to such an extent that the draught is too much restricted. This produces numerous small and constantly changing currents, which prevent any one of the large currents getting the advantage of the others, and thus equalises the draughts.

At some factories the method of working is as follows:—the Glover tower is packed very loosely, and itself acts as a chimney, so that the burners have always very good draught and never blow out, whilst it is quite possible at the same time to keep the exit draught so low that there is some little outward pressure even in the last chamber. In the next chapter an arrangement is described by which this aim can be attained even more perfectly.

Regulation of the Draught.—Something has already been said about the principles according to which the supply of air must be regulated; and this will be referred to in the next chapter; for the present, it is sufficient to state that there must be in any case enough total draught *behind* the chambers, but not too much; otherwise, even if the burners themselves are protected against excess of draught by diminishing the air inlet of the burners, there is all the more tendency for air to enter the chambers from all the other sides through the finest chinks and thus disturb the process. If the draught is excessive, the incubus of the vitriol-maker, pale chambers, at once makes its appearance.

Whether, therefore, the draught is produced by a chimney or by an open pipe, there must always be some contrivance *for regulating* it. At many works this is done by a simple damper, introduced into the lead pipe by a slit, luted with clay or not at all. The arrangement shown in Fig. 72, partly in elevation, partly in section, and in Fig. 73, in cross section, is

far more perfect. The draught-pipe, *a a*, is widened out into a rectangular vessel surrounded by a jacket, *b b*, forming a hydraulic joint; and the damper, *c*, is surrounded on all sides

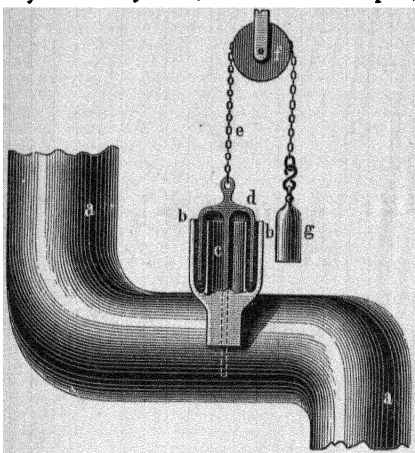


FIG. 72.

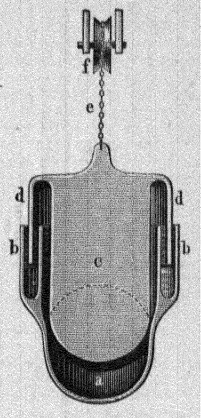


FIG. 73.

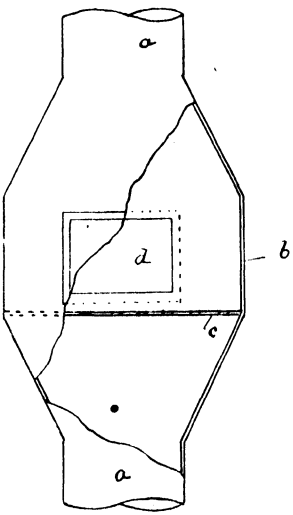


FIG. 74.

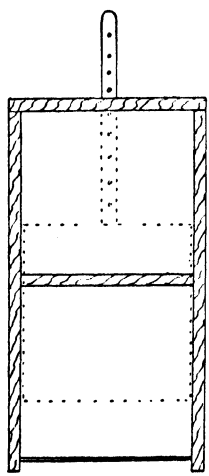


FIG. 75.

by the jacket *d d*, dipping into the water-lute at *b*. The damper is raised and lowered by the help of the chain, pulley, and balance-weight, *e*, *f*, *g*.

In many works the arrangement shown in Fig. 74 is met

with. The draught-pipe, *a a*, is interrupted by a wider portion *b*, divided into two parts by a horizontal diaphragm, *c*. The latter is perforated by a number of holes the total area of which is somewhat larger than that of the pipe, *a a*. When, therefore, all the holes are open, there is no obstacle whatever to the draught; but this can be produced at will by closing a certain number of the holes with lead caps. For this purpose the space above the diaphragm is accessible by a small window, *d*, to which

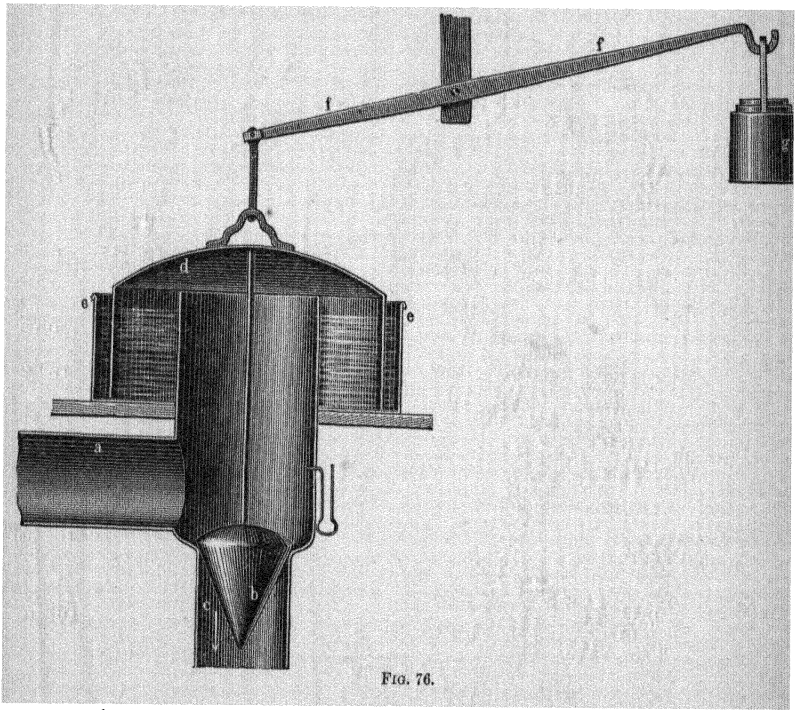


FIG. 76.

another pane on the other side corresponds, so that the whole at the same time serves as a "sight."

Another type of damper for vertical or horizontal flues, square in section, is shown in Fig. 75. It is constructed entirely of regulus metal, but the outside guides may be of iron or wood. The position of the damper is easily fixed by means of a pin placed in one of the holes in the stem.

Automatic Regulation of the Draught in the Chambers.— It is advisable, especially in the case of chambers not connected with a high chimney, where changes of wind, etc., produce great

variations of draught, to adopt some automatic regulation together with the ordinary dampers, etc. This can be made by putting on to the horizontal part of the exit-pipe a perpendicular 12-in. pipe, closed by a bell standing in an annular water-lute. The bell hangs on one arm of a lever, the other arm of which is so weighted that the bell can travel freely. When the draught is just right, this second arm has a certain position, in which a throttle-valve within the exit-pipe connected with it is half open. When the draught increases, the bell descends, owing to the increase of atmospheric pressure, and partly shuts the throttle-valve; in the opposite case of the draught decreasing, the throttle-valve is opened wider. This apparatus, as constructed by M. Delplace, is shown in Fig. 76, where *a* is the entrance-pipe from the Gay-Lussac tower, *c* the exit-pipe, *b* a conical valve, *d* the regulating bell, *e e* the water-line of the hydraulic joint, *f* the lever, *g* the balance-weight.

In Lunge's fourth edition, pp. 750-753, a description with drawings is given of an apparatus of W. G. Styrpe, of Wicklow, which differs somewhat from that just described. The apparatus appears too complicated for ordinary acid plants.

By Fans.

Mention has previously been made (p. 122) of the various drawbacks connected with the application of injectors for producing draught, and several works have adopted the plan, originally followed at Freiberg,[1] of introducing *fans* made of lead alloyed with antimony, or wood or iron covered with lead, fixed on iron axles, running in somewhat tightly fitting lead journals without stuffing-boxes. These fans are arranged either between the Glover tower and the first chamber, or between the last chamber and the Gay-Lussac tower, or in both places.

The systematic production of draught by placing one fan behind the Glover tower and another in front of the Gay-Lussac has been especially worked out by F. J. Falding.[2] These fans

[1] According to Mühlhäuser (*Z. angew. Chem.*, 1902, p. 672), this invention is due to a mining engineer of the name of Hagen, at the Halsbrücke works.

[2] *Cf. Min. Ind.*, 7, 672.

have a cast-iron casing lined with lead, and a spindle and arms made of antimony-lead. They are very carefully mounted, and work up to 700 revolutions per minute.

Niedenführ (1902) considers that a fan would be best placed between the burners and the Glover tower, but he believes this to be impossible with ordinary fans on account of the high temperature of the burner gases.

Usually the fans are made of iron covered with lead, or altogether of "hard lead" or "regulus," but of course the axle or spindle should be made of steel. In very hot places, however, where lead is out of the question, cast-iron may be employed, which is not acted upon so long as no acid is condensed upon it. Here the journals are the weak point, but this has been overcome by A. P. O'Brien, at Richmond, Va., in the following manner[1]:—A cast-iron fan is placed immediately behind the burners, before the nitre-oven and Glover tower. It has 27 in. suction and discharge, and is made of cast-iron throughout, including the spindle, and is covered with a 1-in. coat of asbestos cement. The temperature beside the fan is about 540°. The journals are not oiled, but flooded with water from several $\frac{3}{8}$-in. pipes. Water also surrounds the jacket of each journal, and is admitted to the oil-chamber instead of oil as a lubricant. After nine months' work this fan had not required any repair. No wrought-iron or steel is in contact with the gas.

The B. P. 15293 of 1913, of the British Thomson-Houston Co. (for the General Electric Co. at Schenectady, U.S.A.), describes a centrifugal fan with controllable speed.

Kestner[2] is of opinion that the best place for a fan is behind the chambers. If placed between the burners and the Glover tower, its construction is rendered more difficult on account of the heat and the impurities of the burner-gases. The advantage of increasing the pressure in the chambers by placing it before them is extremely slight, amounting only to about $\frac{1}{2000}$ of the atmospheric pressure. Kestner's fans, of which a large number have been supplied, are usually placed at the end of the chamber-system. They possess a wheel made of antimony-lead ("hard lead") and a case of the same material

[1] Falding, *Min. Ind.*, 9, 621.

[2] *J. Soc. Chem. Ind.*, 1903, p. 333; more explicitly in *Verhandl. V. Kongress für angew. Chem.*, 1905, 623 *et seq.*

or of Volvic lava. They rotate at medium speeds, and are usually driven by a special steam or electric motor. The part played by the fan is not to draw more air through the chambers, but to keep the current of air constant, not influenced by the variations of the atmospheric pressure, temperature, wind, etc. According to *Chem. Zeit.*, 1910, p. 734, Kestner has

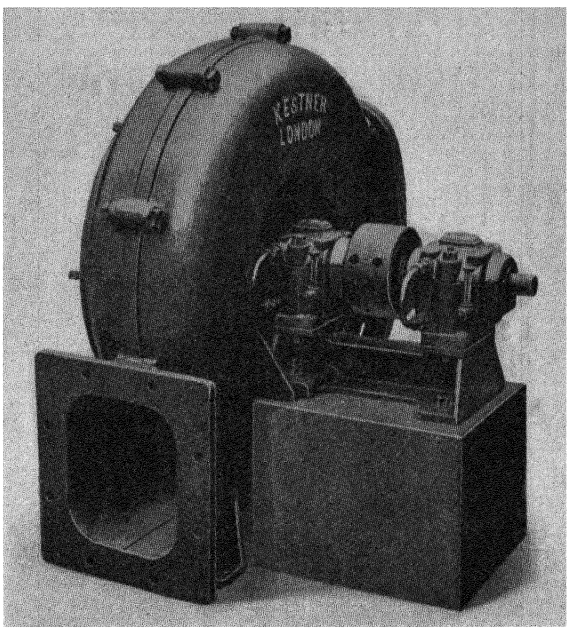


FIG. 77.

increased the usefulness of his hard-lead fans by a special construction with back-suction for hot gases and high pressures.

According to a communication from the Kestner Engineering Co., Ltd., 5 Grosvenor Gardens, Westminster, S.W.1, over 1000 of their hard-lead fans are working all over the world. It is specially pointed out that they are very durable, and require very little power for driving. They are now made for temperatures up to 125° and working-pressures up to 250 mm., and are employed for acid-chambers and tower-systems.

Kestner has also made a special type of fan which is placed between the burners and the Glover tower. It is built entirely of

cast-iron where it comes in contact with the gases, and a very efficient method of water-cooling is adopted for the bearings, so that the lubricating oil is kept cool, and there are no difficulties in this direction. The speed of this fan is not high, so that it can be arranged for long and continuous running without undue heating of the bearings.

Fig. 77 shows the low-pressure "C" type, which are made in the following sizes and capacities:

Nos.	Diameter of suction. inches.	Capacity in cubic feet per min.	Normal speed revolutions per min.
40	16	2310	880
45	18	2940	750
50	20	3630	650
55	22	4600	620
60	24	5600	500
70	28	8000	420

The "S" type of low-pressure fan is shown in Fig. 78, and is suitable for placing between the Glover tower and the first chamber. They are made in the following sizes and capacities:

Nos.	Diameter of suction. inches.	Capacity in cubic feet per min.	Revolutions per min.
30	12	730	800
35	14	1100	700
40	16	1450	620
45	18	1950	560
50	20	2550	500
55	22	2990	450
60	24	3350	400
70	28	5400	350

In this case, the temperature being high, Kestner adopts his special construction in which the impeller blades are built of steel with a homogeneous coating of lead. This type of impeller can stand the highest temperatures found in this position. For the fan at the end of the set, the type used has an impeller built of solid regulus. In all these fans, a balancing

pipe is arranged, which has the very useful function of preventing any gases being drawn up at the point where the shaft passes through the casing.

Benker (1902) always employs fans (and water-sprays) for "high-pressure work."[1] He places the fans preferably between two Gay-Lussac towers; if there is only one Gay-Lussac, the fan is placed behind this, but is followed by a small tower fed

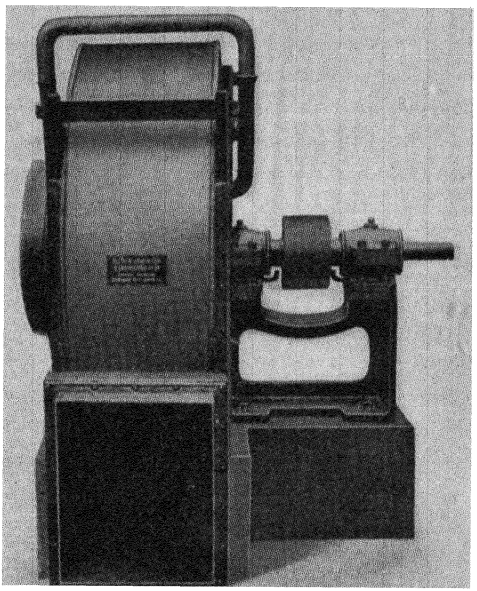


FIG. 78.

with water in order to condense the acid mist. The object of the fan is to avoid the inequalities and temporary losses of draught, caused in the case of chimneys by wind, etc., and to produce a regular composition of the exit-gases. As there is a difference of temperature between day and night, the speed of the fan must be regulated at least twice a day. Benker states that attempts at placing a fan between the Glover tower and the first chamber were not successful, principally on account of the necessity of frequent repairs, although even shells made of Volvic lava were tried.

The question of employing fans for acid-chambers has

[1] *Cf.* p. 45 *et seq.*, and Chapter III.

received a new impetus by Niedenführ's Ger. P. 140825, which provides two Glover towers in succession, to fulfil separate functions, the fan being placed between them. This question will be treated in the next chapter, when discussing the functions of the Glover tower.

Lüty [1] strongly approves of the use of fans, especially in the way adopted by Niedenführ, but this is strongly contested from other sides.

Rabe [2] discusses at length the part which fans play in the lead-chamber process. This is merely the task of overcoming the friction in the single parts of the apparatus. It is not correct to speak of an "increase of draught," since the pressure is increased behind the fan as well. It is merely an apparatus for moving the gases from one side to the other. The velocity of the gas on the side of aspiration is essentially the same as on the side of pressure, although the pressure is different on the two sides. Hence, it is quite immaterial for the movement of the gas in which place the fan is put, whether in front of the burners (which has certain advantages), or in front of or behind the Glover, or at the Gay-Lussac, or anywhere else. It is impossible to influence the gas on *one* side of the fan only. But, of course, certain reasons exist for placing the fan in one or the other of those places. If it is required to bring the fan into contact only with pure air, it must be placed in front of the burners, which in this case, of course, must be provided with a closed air-conduit. If the fan is sufficiently resistant to hot acid gases, it is placed in front of the Glover (Falding's system). If, however, it is to be in contact only with *cold* acid gases, these must be previously cooled. The performance of the fan in overcoming the friction in the various parts of the apparatus makes it possible either to employ apparatus offering greater resistance to the current of gas, or to pass more gas through the chambers than can be done by natural draught. In the former case, apparatus for precipitating the flue-dust, for utilising the heat, and generally for making the chamber-process more rational, may be interposed in already existing plant, without in any way diminishing the quantity of the gases. In the second case, the velocity of the gaseous current may be

[1] *Z. angew. Chem.*, 1905, p. 1253 *et seq.*
[2] *Ibid.*, 1905, p. 1735 *et seq.*

increased, and this, of course, means an increase of the production of the chambers. In these cases as well it does not matter where the fan is interposed, since in most descriptions of fans it is immaterial whether the greater resistance takes place in the aspirating- or in the pressure-conduit.

The regulation of the work of the fan is best performed by changing the number of revolutions, or, where this is impossible, by throttling. In any case, the aim should not be that of producing a certain plus- or minus-*pressure* against that of the atmosphere, but that of producing a certain *velocity* of the gases, as shown by instruments indicating this, since these are independent of any obstructions in the gas-conduits, etc., and since it is important to work with gas of a uniform percentage of SO_2. Of course, it is also desirable to observe the pressure in every part of the apparatus, as this admits of early recognising the constancy of the friction exerted. Thus the chamber work is more easily controlled, and the velocity of the gas current can be kept constant as long as there is an excess of power in the fan. Of course, it is not permissible to work the fan in such a manner that the towers or chambers are damaged by an excess or a deficiency of pressure against that of the atmosphere. In the case of new plant it is best to effect, from the outset, the smallest possible friction in the apparatus and conduits, for fans work more economically with small differences of pressure. It is impossible to render the roasting and the chamber-process independent of each other, but it is possible to make the work independent of the resistance by friction, whether this be permanent or produced in the course of working. Nor can the absolute pressure within the chambers be essentially altered; the places immediately in front and in the rear of the fan may show differences of, say, 50 mm. water-pressure, but the more remote parts show much less, down to 0·025 per cent. of the atmospheric pressure, which is altogether insignificant in comparison with the variations of atmospheric pressure, which may reach 2 per cent. The propulsion of the gases is precisely the same whether there is a plus- or a minus-pressure, both in the Glover and in the chamber, other circumstances being equal. It is erroneous to assume that a plus-pressure by itself is essential for the movement of the gases, or that such a pressure forces the gases to penetrate into every

part of the apparatus and to avoid "dead corners." It is certainly true that the best utilisation of an apparatus depends to a great extent upon the way in which the gases travel through it, so that it is very important to find out the best conditions; but it is quite unessential whether this work is done by plus- or by minus-pressure. In working with fans, gyratory motions have been spoken of as taking place, but these occur precisely in the same way with plus- or with minus-pressure, and they cease in longer conduits. If the higher pressure by itself produced the effects assumed, the same differences would appear without fans between factories situated at a higher or lower level, and the daily oscillations of atmospheric pressure would influence the working of the chambers to an alarming extent. Every chamber manager knows that he must take account of these, but his task is not to increase the plus- or minus-pressure, but to regulate the velocity of the gas so that the proportions by *weight* are kept constant. The plus- or minus-pressure has nothing to do with this; the reactions are essentially the same in both cases; neither is there a special movement of the gases, nor a more intimate contact of the molecules, and the alleged proofs for the contrary are not correct. The results adduced by Lüty[1] are much better explained by differences in the size of the apparatus, the style of work, the cooling action, etc., and they have nothing to do with the place given to the fan.

M. Neumann[2] criticises the plan of Niedenführ (Ger. P. 140825, *vide* p. 132) and Lüty's remarks upon it (*ibid.*). Schliebs[3] has had most favourable experience with fans placed between the Glover and the first chamber. He further advocates his view.[4]

Niedenführ[5] replies to Rabe and to Neumann. The velocity of the gaseous current ought to be as uniform as possible, beginning with the burners; hence the resistances should be reduced as much as possible and not vary very much. This leads to placing the fan as nearly as possible behind the burners, where it can best act against the causes of changes in the composition and velocity of the gases. The same considera-

[1] *Z. angew. Chem.*, 1905, p. 1253 *et seq.*
[2] *Ibid.*, p. 1814 *et seq.*
[3] *Ibid.*, p. 1900 *et seq.*
[4] *Ibid.*, 1906, p. 571.
[5] *Ibid.*, p. 61 *et seq.*

tion leads to a throttling of the outlet from the Gay-Lussac tower, which takes place best behind a second fan, placed there. Most sulphuric-acid factories now work with fans, and the writer has always found the best results by placing the fan in front of the first chamber. This conclusion, identical with the ideas of Lunge and Falding, has been verified by experiments made with tangential chambers.

Hartmann and Benker [1] criticise a number of the statements and opinions put forward by the preceding authors, and again insist on placing the fan at the end of the system, between the two Gay-Lussacs, or, if there is only one such tower, between it and the last chamber. They consider it wrong to place it in front of the Glover, except in the case of mechanical burners, where this is just the right place for a fan ; but then they put a second fan at the end of the system (like Falding). In the case of ordinary burners for lumps or smalls the upward draught of the gases is sufficient by itself to send them into the chambers ; if increased by a fan, placed between the burners and the first chamber, the pressure is too great and the life of the chamber is considerably shortened, and much flue-dust gets into the Glover, or even into the chamber. If the fan is placed at the end of the system, in front of the last Gay-Lussac, the gases enter it cold and dry, and the fan is not damaged ; it can be mounted below the tower and without stopping the work, and is easily accessible for repairs. In this place it is most efficient for overcoming the frictional resistance of the Gay-Lussac tower, as well as the difficulties caused by changes of the atmospheric conditions.

Th. Meyer [2] defends his "tangential system" and the necessity of placing the fan *in front* of the tangential chamber, behind the Glover.

Processes for special methods of introducing the gases into the vitriol-chambers will be mentioned later on, *e.g.* Rabe's Ger. P. 237561, for aiding their movement according to Abraham's "spiral" theory.

[1] *Z. angew. Chem.*, 1906, pp. 132 to 137.
[2] *Ibid.*, pp. 523 to 525.

Anemometers.

An anemometer adapted for controlling the draught in vitriol-chambers is the Péclet's *differential anemometer* as modified by Fletcher and Swan. It is based on the physical principle that a current of air passing the open end of a tube causes a partial vacuum in the tube. If, therefore, a straight tube is introduced through a hole into a chimney, or into the draught-pipe taking away the chamber-gas, so that the gaseous current passes the open end of the tube at right angles, a partial vacuum, proportional to the velocity of the current, will be formed in the latter; but the aspirating action of the chimney will be equally communicated to this tube. To distinguish between these two actions, two tubes must be introduced into the chimney, one of which ends straight, whilst the other is bent to a right angle, so that the current of air blows into it. Both tubes will now be affected by the aspirating action of the chimney. In the straight tube this is *increased* by the aspirating action of the current crossing its open end, whilst in the bent tube it is diminished by the air blowing into it. The difference between the aspirating action of the two tubes is thus reducible to the action of the current of air, and by measuring this the speed of that current can be ascertained. For this purpose the two tubes are connected with a U-shaped glass tube containing water or another liquid, which will rise in one of the limbs to an extent corresponding to the difference of suction. Since the sucking-action of the chimney acts upon both limbs, it is eliminated, and the difference of level corresponds merely to the different action exerted by the current of air upon the straight tube, which it crosses, and the bent one, into which it blows. This action increases and diminishes with the speed of the current, which can accordingly be deduced from it. Water (used by Péclet), on account of the friction in the U-tube, is adapted only for currents of a greater speed than 5 ft. per second. Fletcher overcame this difficulty thus:—In order to lessen the friction, he employed two cylinders *a a'* (Fig. 79), of 4 in. diameter, connected at the bottom by a narrow tube *b*. This arrangement is ten times as sensitive as a U-tube of 0·4 in. width would be, since the area upon which the pressure acts is increased 100-fold, but the circumference upon

which friction acts only 10-fold. The rising and falling of the liquid is observed by means of metal floats *c c*, upon which a very fine horizontal line is marked. The scale *d* provided with a vernier and a very fine adjusting-screw, permits the difference of level, down to $\frac{1}{1000}$ part of an inch, to be read off. This is possible, if ether is used instead of water. The two glass tubes *e* and *f* are inserted into the draught-pipe, at right angles to the current of gas (so that it blows into the bent tube *f*), and are connected by elastic tubes *h i* with *a a'*.

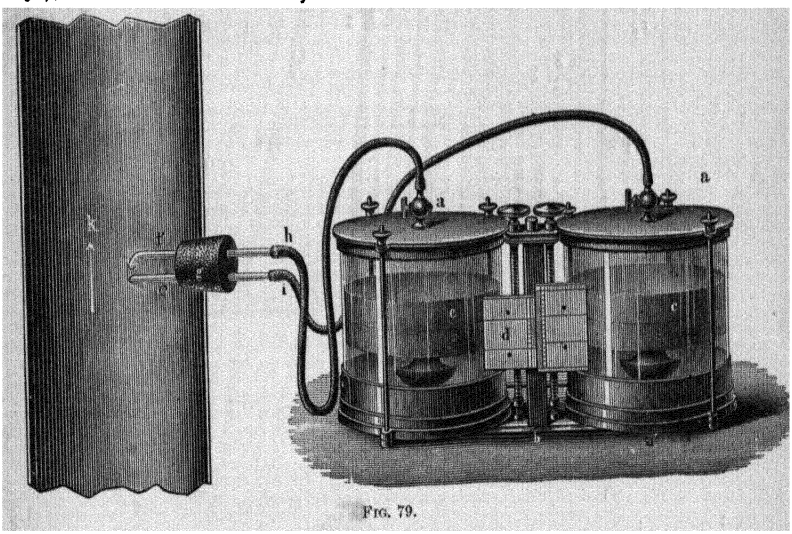


FIG. 79.

This form of anemometer has been simplified by Lunge, and is shown in his third edition, p. 564, Fig. 244.

This instrument is not influenced by soot, heat, or corrosive vapours. It can be placed at some distance from the flue to be tested, if longer rubber tubing be used. It can, of course, be employed both for aspirating and for pressure currents (fans, etc.), and as a measure for the speed of atmospheric currents.

Of course, like every other anemometer, Fletcher's only indicates the pressure at the place occupied by its receiving portion. Accordingly the tubes *e* and *f* must be introduced far enough to reach into the air-current to the extent of about one-sixth of the diameter of the flue. The velocity at this place is assumed to be nearly equal to the average. This is, however, very doubtful, and there are no means at present

known of measuring the absolute quantities of air passing through a flue of any considerable sectional area with any degree of accuracy.

Fletcher's anemometer has been improved by Swan in the following way, which is practically a return to Péclet's original construction.[1] Instead of the 4-in. cylinders he takes a U-tube of $\frac{1}{8}$ in. diameter, narrowed at the bend to diminish the oscillations. The tube is 10 in. long, and placed with an inclination of 1 : 10. Each limb has a scale and vernier, the latter partly made of glass and covering at the same time the scale and the tube, so that it is easy to read off to $\frac{1}{100}$ in. The ends of the tube are connected with a two-way cock, so that the current

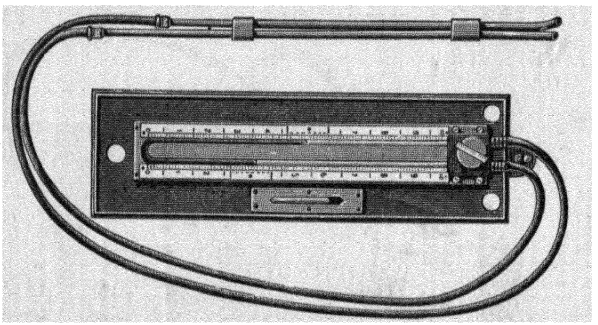


FIG. 80.

can be reversed without opening any joint. Fig. 80 shows the instrument as seen from above, so that its inclination to the vertical does not appear. It is fixed on a stand provided with a spirit-level and adjusting-screws. It is employed just like Fletcher's anemometer, but, owing to the inclination of 1 : 10, the column of ether in the tube is ten times as long for the same difference in pressure, and the reading of $\frac{1}{100}$ in. gives thus the same result as the more difficult one to $\frac{1}{1000}$ in. in Fletcher's instrument. The narrowness of the tubes does not matter in the case of ether, as the friction may be entirely neglected with this substance (the later form of Fletcher's anemometer, shown in Fig. 79, bears this out as well). Swan's anemometer must always be placed exactly level in the direction of its length; but it need not be levelled across, if a reading be made in one limb, the two-way cock turned, and the new reading in the

[1] A similar plan has been independently proposed by P. Hart, *Chem. News*, **21**, 200.

same limb subtracted from the first; thus it is unnecessary to read off at both limbs, which would involve levelling across as well.

Other instruments for measuring the draught are, for instance, those of Kretz,[1] of Ramsbottom,[2] of Scheurer-Kestner,[3] none of which can vie with Fletcher's in sensitiveness. The very ingenious anemometer of Hurter[4] is only adapted for laboratory use. *Cf.* also Bourdon's multiplying anemometer.[5]

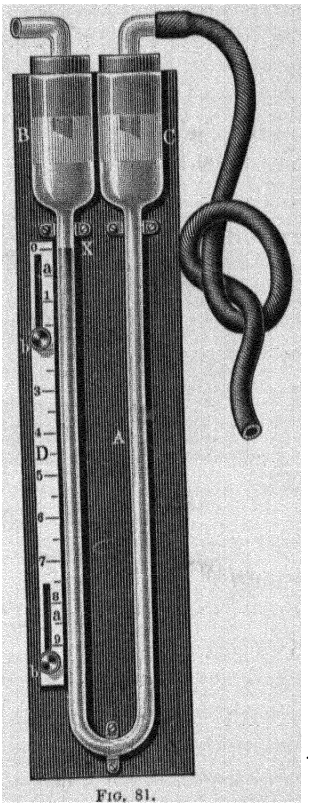


FIG. 81.

One of the most delicate anemometers is Fryer's, described in the *Inspector's Report on the Alkali Acts for 1877-1878*, p. 68. Its principle is to measure the difference of pressure on each side of a copper plate shaped like a watch-glass and connected with a spiral spring. It will measure a pressure of $\frac{1}{3000}$ of an inch.

Recently differential anemometers on another principle have come very largely into use, and seem to be preferable to all others. There are already a good many forms of this apparatus, one of the best known being that of Professor Seger (Ger. P. 19426), shown in Fig. 81. The calibrated U-tube A is surmounted by two cylindrical cups, B and C, of equal width. The board on which it is fastened also carries the sliding-scale D, adjustable by slits *a a* and screw-pins *b b*. The tube is filled with two non-miscible liquids—for instance, heavy paraffin oil and dilute, coloured spirits of wine—of nearly equal specific gravity, to such an extent that the zero-point of the scale D can be put exactly at the line of contact of the

[1] *Dingl. polyt. J.*, 190, 16.
[2] *Ibid.*, 180, 334.
[3] *Ibid.*, 206, 448, and 221, 427.
[4] *Ibid.*, 229, 160.
[5] *Comptes rend.*, 94, 5; *J. Soc. Chem. Ind.*, 1882, p. 60.

liquids at X. If an aspirating force acting on the surface of the liquid in C raises the level in that part of the tube a certain distance, the point X will fall this distance multiplied by the ratio of the sectional area of C to A. If, for instance, the ratio of the sections is as 20 : 1, a difference of pressure of 1 mm. will be indicated on the scale by a sinking of X to the amount of 20 mm. The scale is graduated in such a

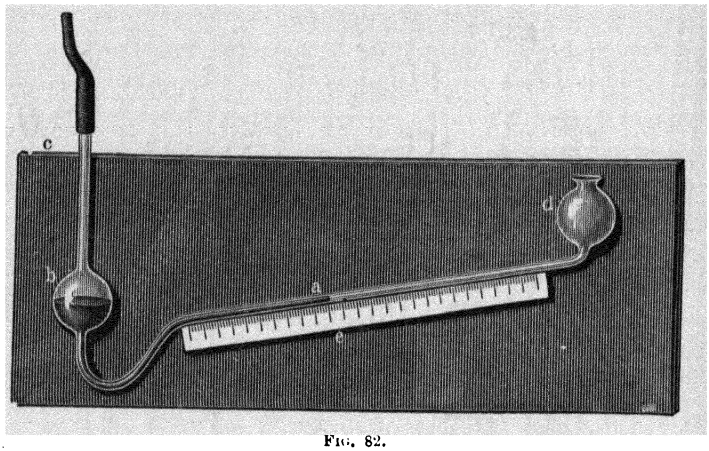


FIG. 82.

way that it indicates the pressure expressed in millimetres of water. This instrument is much cheaper and easier to handle than those constructed on Péclet's principle, and quite as accurate.

A very sensitive *pressure-gauge* has been described by Vogt.[1] The pressure is observed by the movement of a small air-bubble contained in a horizontal glass tube of 4 or 5 mm. diameter. The glass tube, besides this bubble, is filled with water or another liquid, and is connected on each side with a bottle tubulated near the bottom. One of these bottles is 15 to 16 cm., the other 6 to 8 cm. wide; the liquid stands at the same level in each. The pressure within the lead-chamber is made to act upon the surface of the liquid in one of the bottles, and its amount measured by the position of the air-bubble. The apparatus is all the more sensitive the greater the difference between the diameter of the tube and that of the bottles. There is a contrivance for admitting a bubble of air previous

[1] *J. prakt. Chem.*, 14, 284.

to using the apparatus, and for again equalising the levels after use.

A very simple pressure-gauge, sufficiently sensitive for ordinary purposes, is shown in Fig. 82.[1] The tube *a* has an inclination from the horizontal of 1 : 10; it is connected with a reservoir *b* 1½ or 2 in. wide, upon which the pressure is brought to act by the rubber tube *c* (if there is suction, the vessel to be tested must be connected with the bulb *d*). The gauge is filled with a mixture of water and spirit of wine coloured with magenta or otherwise. As the movement of the liquid in the bulb *b* can be neglected, any movement of the liquid in the tube *a*, as measured on the scale *e*, corresponds to one-tenth of its extent in real height. If, for instance, each degree on the scale is = $\frac{1}{10}$ in., it indicates a real pressure of $\frac{1}{100}$ in. It is best to cause the liquid to move before each observation, in order to wet the tube.

The measurement of the velocity of a current of gas can be carried out by measuring the pressures before and behind a throttling arrangement interposed in the conduit-pipe. The instrument of H. Rabe (Ger. P. 111019), described in *Z. angew. Chem.*, 1900, p. 236; 1901, p. 950; 1903, p. 136, is constructed on this principle.

General Remarks on the Measurement of the Draught.

Rabe[2] draws attention to erroneous ideas frequently entertained on the indications given by pressure-gauges and anemometers. It is a mistake to assume that the velocity of a gaseous current can be directly inferred from the indication of the pressure-gauge. This merely shows the difference of pressure between the apparatus to which it is attached and the outer air. It is different with "anemometers" like those described above, where *both* limbs of the instrument shaped in a special way are introduced into the apparatus, whereas in ordinary pressure-gauges only one of the limbs is connected with the apparatus to be tested. By "velocity of the current of gas" is meant the volume of gas which passes through unit volume of the apparatus in unit time: *e.g.*, if 10 cub. m. of

[1] From Sorel, *Industries Chimiques*, p. 142.
[2] *Z. angew. Chem.*, 1905, p. 1735.

the gas pass through 1 cub. m. of the apparatus in one second, this is spoken of as the gas-velocity = 10; it does not matter whether the conduits are wide or narrow, and whether the apparatus is empty or filled with packing, since only the space really occupied by the gas is taken into consideration. Nor does any throttling change the proportional velocity of the gas in the parts in front or behind, since the movement takes place on both sides of the throttling-valve. It is, therefore, immaterial in which part of the chamber-system the throttling takes place, whether before the air enters the burners, or where the gases enter the chambers, or between the single chambers, or in front of or behind the Gay-Lussac; in every case the *whole* of the gas is influenced in the same way, in spite of the different view of many "practical" men. These considerations also apply to the action of the fans spoken of *supra* (p. 120 *et seq.*).

Calculation of the Volume of Chamber-gases according to Temperature and Moisture.

In all calculations concerning chamber-gases it is not sufficient to take into account the difference of temperature and barometric pressure from the normal state of 0° and 760 mm., but the amount of moisture present in the chamber-atmosphere must be equally brought into the calculation. It is evidently impossible to do this on the assumption that the tension of aqueous vapour within the chambers is that ordinarily existing for any given temperature. The presence of sulphuric acid, not merely at the bottom but all over in the form of mist, greatly changes the aqueous-vapour tension according to the varying strength of the acid. The tables of Regnault and Sorel, given on pp. 214 and 215 of Vol. I, would admit of making the calculation in the proper manner; but it will be more convenient to consult the table on p. 143 (calculated by Sorel), which gives at once the *volume occupied by a cubic metre* (or cubic foot) *of air, originally at* 0° *and* 760 *mm. pressure, after being brought into equilibrium of temperature and vapour-tension with dilute sulphuric acid of varying strength and temperature,* but without any change of pressure.

Percentage of H_2SO_4 in the acid.	10°.	15°.	20°.	25°.	30°.	35°.	40°.	45°.	50°.	55°.	60°	65°.	70°.	75°.	80°.	85°.	90°.	95°.
44	1·042	1·063	1·085	1·108	1·133	1·160	1·192	1·225	1·263									
46	1·042	1·062	1·084	1·107	1·131	1·157	1·188	1·218	1·256	1·303	1·356	1·427						
48	1·042	1·062	1·083	1·105	1·129	1·155	1·185	1·212	1·249	1·292	1·341	1·397	1·478	1·542				
50	1·041	1·061	1·082	1·104	1·128	1·152	1·180	1·207	1·241	1·281	1·327	1·377	1·452	1·509	1·589	1·756	1·911	
52	1·041	1·060	1·081	1·103	1·125	1·150	1·177	1·202	1·234	1·270	1·313	1·359	1·429	1·478	1·562	1·662	1·830	2·014
54	1·040	1·060	1·080	1·102	1·122	1·147	1·175	1·198	1·227	1·260	1·301	1·343	1·408	1·449	1·526	1·625	1·752	1·904
56	1·040	1·059	1·079	1·100	1·121	1·144	1·169	1·194	1·222	1·252	1·290	1·328	1·388	1·423	1·490	1·589	1·684	1·813
58	1·039	1·059	1·078	1·099	1·120	1·142	1·166	1·190	1·215	1·244	1·279	1·313	1·369	1·400	1·456	1·534	1·625	1·734
60	1·039	1·058	1·077	1·098	1·119	1·140	1·163	1·186	1·209	1·237	1·269	1·299	1·352	1·368	1·428	1·495	1·575	1·668
62	1·038	1·058	1·077	1·097	1·118	1·138	1·160	1·182	1·204	1·230	1·261	1·289	1·335	1·357	1·402	1·462	1·532	1·613
64	1·038	1·057	1·076	1·096	1·117	1·136	1·158	1·178	1·200	1·224	1·253	1·279	1·322	1·337	1·379	1·431	1·493	1·562
66	1·038	1·057	1·076	1·095	1·116	1·135	1·157	1·175	1·197	1·219	1·246	1·271	1·311	1·324	1·362	1·408	1·464	1·522
68	1·038	1·056	1·075	1·095	1·114	1·134	1·156	1·173	1·194	1·215	1·239	1·263	1·302	1·316	1·347	1·388	1·437	1·488
70	1·038	1·056	1·075	1·094	1·114	1·133	1·155	1·172	1·192	1·212	1·235	1·258	1·293	1·308	1·338	1·366	1·412	1·456
72	1·038	1·056	1·074	1·094	1·113	1·132	1·153	1·171	1·191	1·210	1·232	1·254	1·289	1·302	1·330	1·344	1·391	1·429
74	1·037	1·056	1·074	1·093	1·112	1·131	1·152	1·170	1·190	1·209	1·229	1·251	1·284	1·296	1·321	1·340	1·374	1·407
76	1·037	1·055	1·074	1·093	1·111	1·131	1·151	1·169	1·189	1·208	1·227	1·248	1·280	1·291	1·313	1·337	1·362	1·388
78	1·037	1·055	1·074	1·092	1·111	1·130	1·150	1·168	1·188	1·207	1·226	1·246	1·277	1·287	1·307	1·330	1·352	1·376
80	1·037	1·055	1·073	1·092	1·110	1·130	1·149	1·167	1·187	1·206	1·225	1·245	1·275	1·284	1·303	1·324	1·345	1·367
82	1·037	1·055	1·073	1·091	1·110	1·129	1·149	1·166	1·186	1·205	1·224	1·244	1·274	1·282	1·300	1·318	1·339	1·359

CHAPTER II

THE RECOVERY OF THE NITROGEN COMPOUNDS

THE recovery of the nitrogen oxides which are still present in the gaseous mixture issuing from the last chamber, has been previously mentioned as a process indispensable for the rational manufacture of sulphuric acid. It saves not merely at least two-thirds of the nitre, but also a great deal (a quarter up to a third) of the chamber-space. It increases the yield of sulphuric acid, and, moreover, prevents the escape of acid fumes into the atmosphere. Several processes may be employed for this object, but, with one exception, they only require to be briefly mentioned. The only plan which has turned out successful in manufacturing practice, and which, certainly after a considerable length of time, has been introduced into all well-managed works, is that which was proposed by Gay-Lussac as early as 1827, viz., the *absorption of the nitrous fumes by strong sulphuric acid.* The chemical fact underlying this process, viz., the behaviour of the oxides and acids of sulphur and nitrogen towards one another, has been fully discussed on p. 249 *et seq.* of Vol. I, and can be referred to there. An examination will here be made of the technical means employed for recovering the greater part of the nitre contained in the exit-gases from the vitriol-chambers; only the following reactions, therefore, need be repeated here.

Moderately concentrated sulphuric acid absorbs no *nitric oxide* from gaseous mixtures, except in the presence of oxygen, when of course higher nitrogen oxides are formed. *Nitrous acid* is absorbed with the formation of nitrososulphuric acid:

$$2H_2SO_4 + N_2O_3 = 2SO_2(OH)(ONO) + H_2O.$$

Nitrogen peroxide is absorbed with formation both of nitrososulphuric acid and of nitric acid;

$$H_2SO_4 + N_2O_4 = SO_2(OH)(ONO) + HNO_3.$$

Nitrososulphuric acid is *decomposed* by water alone:

$$2SO_2(OH)(ONO) + H_2O = 2H_2SO_4 + N_2O_3,$$

or by water and SO_2:

$$2SO_5NH + SO_2 + 2H_2O = 3H_2SO_4 + 2NO.$$

The *apparatus* most frequently used *for retaining the nitrous fumes* by means of strong sulphuric acid is the *coke-tower* mentioned above, and justly designated everywhere by the name of its inventor. From the facility with which this apparatus retains at least two-thirds of all the nitre, and from the other important advantages realised by it, it might have been expected that it would have been generally introduced within a short period after its invention. But, most curiously, Gay-Lussac's invention was carried into practice for the first time only in 1842, at Chauny; and forty years after its invention the majority of sulphuric-acid makers did not possess either Gay-Lussac's or any other apparatus for retaining the nitrous fumes. Even some of those who adopted the Gay-Lussac in the first instance abandoned it later.

The cause of this was that formerly the only practicable plan of recovering the nitre from the nitrous vitriol obtained in the Gay-Lussac tower consisted in diluting it with water, and the expense of reconcentrating and of pumping the acid, etc., was thought to amount to nearly as much as the saving of nitre. Most manufacturers were not aware that the saving (which was mostly estimated too low, viz., equal to one-half of the nitre) was not the only advantage of the absorbing-towers. But the great dearth of nitrate of soda which occurred about the years 1868-1870 brought the matter vividly before them. At the same time, on the Continent, the composition of the chamber-gases, the chamber-space, etc., were studied more closely, and the advantage of an excess of nitrous gas in the chambers, which can only be secured by means of an absorbing-tower, became evident. These circumstances led to the erection of many Gay-Lussac towers, especially as some of the manufacturers who had not given them up had done very well with them.

In England, where the theoretical part of the subject had received much less attention, another practical invention had in the meantime been made, which entirely removed the only

essential drawback of the Gay-Lussac absorbing-tower, viz., the necessity of reconcentrating the acid after denitrating it by dilution; this was the *Glover tower*. Whilst about 1870 only a comparatively small number of English works absorbed their nitre-gas at all, since then all the larger and better works have introduced the Gay-Lussac absorbing-tower, nearly always together with Glover's denitrating-tower. Some few exceptions, however, still survive.

The Gay-Lussac Tower

This apparatus consists of a column placed at the end of the chambers, the walls being made of a material capable of resisting sulphuric acid, and the interior space filled with material presenting a large surface.

It should be made no wider than is necessary in order that the draught may not be impeded by the packing, and the necessary volume of the packing should be obtained by making the tower so much higher.

A considerable vertical height of the absorbing medium can, of course, be obtained by placing two towers alongside each other, and compelling the gas leaving the first tower at the top to pass downwards in order to ascend the second tower; in this case, the acid run down the second tower is pumped up and fed to the first tower. An inefficient arrangement is described in many books and is found in a few badly arranged works, where, from mistaken economy, the absorbing-tower is made of twice the usual horizontal section, and divided into two halves by a partition, in order to pass the gas up one half and down the other. The saving in cost as against two towers or a tower of double the height is not very considerable. On the other hand, that half of the tower in which the gas has to descend is almost entirely sacrificed, because here, where the gas and the liquid travel in the same direction, their mutual action, as experience shows, is negligible. Both gas and liquid travel downwards without coming into intimate contact, and thus arrive at the bottom almost unchanged. The arrangement of a double tower is inadmissible unless the partition extends right through, and the gas issuing from the one division passes downwards by a special pipe, and is allowed to

ascend again in the second division, and thus to *meet* the acid. This answers the same purpose as placing two towers alongside each other.

As far as the *width* of the Gay-Lussac tower is concerned, it should be considerably wider than an empty tube of sufficient diameter for the current of gas, not merely because the packing of the tower occupies a large portion of its section and only leaves a small portion of it as clear space, but also because the packing must be purposely arranged so as to divide the current of gas into a great many separate jets, constantly changing their direction, so as to expose them to the largest possible amount of *contact* with the surfaces of the packing wetted with the absorbing-liquid. The tower must therefore be wide enough to take account of this purposely increased friction. Furthermore, it has to be considered that the *slower* the current of gas, the longer will be the time afforded for the action of the absorbing-liquid, and the more perfect will that action be. This would point to giving the tower as wide a section as possible, in order to slacken the speed of the gaseous current. As, for the reasons stated above, this plan has various drawbacks, the inference is that a middle path should be taken: the tower should be made wide enough not to hinder the draught, and to leave sufficient time for the contact of the gas and the liquid, but not so wide that the liquid cannot be spread equally all over and that the gas can go past it. Evidently no exact calculations can be made as to the proper width; experience only can decide this point. Formerly it was assumed that ordinary coke-packed Gay-Lussac towers ought not to exceed 7 ft. in width in order to secure a uniform distribution of the gas and the acids, but later on towers up to 14 ft. wide have been erected and no drawbacks are reported to have been caused by this extreme width.

The dimensions of the Gay-Lussac tower necessarily correspond to those of the set of chambers to which it belongs, and, of course, much depends upon the type of packing used. In the case, however, of towers packed with coke, their cubic contents should be at least 2 per cent. of the chamber-space.

Undoubtedly a larger absorbing-space permits working with a larger economy of nitre. In the case of large sets this space will usually have to be divided into two towers.

The *foundations* of the tower must, of course, be very substantial, and, if possible, constructed in such a way that any acid running over will not damage them. It is preferable to place the towers high enough to avoid the gas from the last chamber having to descend towards the tower. If, however, the chambers are very high above the ground, this would involve considerable difficulty and expense, and the tower is then raised only high enough above the ground to leave a natural fall from its bottom to an acid-tank, and from this to the pumping-apparatus for the nitrous vitriol.

The foundations usually consist of a solid block of brickwork, reinforced concrete, or stonework, or else of two strong pillars surmounted by an 18-in. arch. Sometimes cast-iron columns are employed, on which are placed iron girders, and crossways on these, iron T-shaped bearers (usually railway-rails), close together so as to form a continuous platform. These (as well as any brick- or stonework) must be well painted with tar, and must be covered at the top by a leaden apron, which directs all the drips past the pillars into a safe place, where the foundations or pillars cannot be touched by it. (The same plan should be followed for the foundations of Glover towers.)

The *framework* of Gay-Lussac towers is now generally made of angle-iron, but in the earlier days was usually made of timber. In the case of towers of an angular section these frames are constructed in the usual way, as is seen in the drawings. (See below.)

The frame must be kept clear of the lead, just as in the case of the vitriol-chambers (p. 14); this, of course, is even more necessary in the case of the Glover tower (see below).

The *shell* of the Gay-Lussac tower is made of *lead*. The lead in Continental works is sometimes unnecessarily thick, from 14 to 28 lb. to the square foot; in British works it is often no more than 7 lb. or even 6 lb. to the square foot, like the chamber-lead. It is, however, better to make the tower of 8 lb. lead, the bottom being a few pounds stronger. There is no reason why the lead should be stronger than this. The gas as well as the acid in this apparatus is only moderately warm. The lead sides are always supported by a frame. Both *circular* and *square* towers are employed; the former taking less lead for the same area.

When coke is used as packing, the towers are frequently lined with tiles or bricks, which are put in dry along with the packing. The object of this lining is to prevent the coke, when it settles down, from cutting the lead, but this lateral pressure can only be provided against by making the lining 9 in. in thickness, or by placing extra supports between the ordinary cross-bars.

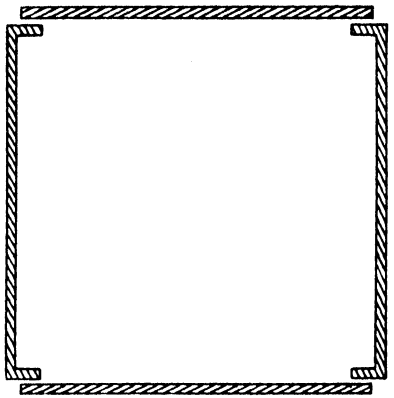


Fig. 83.

In the case of square towers, the sheets forming the sides should be in one piece from top to bottom. They are best put up by placing the roll of lead on the level of the tower-bottom (after having previously fixed the straps); then by winding up, the sheet unrolls, and afterwards the straps can be fastened down. This is a much safer plan than hoisting the whole roll of lead to the top and allowing it to unroll, gradually fixing the straps.

The sheets forming two sides should be turned over at the corners in order to make a joint with the other sheets (Fig. 83). The overlaps of the seams must, in every case, be placed outside (also in the case of the Glover tower), otherwise they would be quickly destroyed. The bottom is made of a single sheet, the four edges being turned up to form the upstand. The corners are cut out and burnt, or simply folded up as shown in Fig. 84.

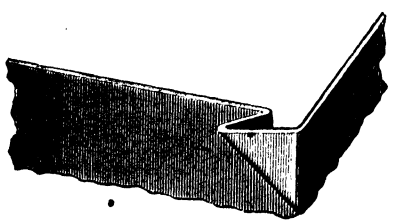


Fig. 84.

Circular towers are usually built with four, and up to eight, uprights of angle- and channel-iron, to which are attached the circular angle-iron rings *a*, Figs. 85 and 86.

After the strong lead dish *b* has been placed on the base *c*,

prepared for it, the erection of the lead shell can be proceeded with. A hollow drum of wood is constructed, of somewhat smaller diameter than the tower, and of a depth equal to the distance between the horizontal rings just mentioned. The lead is now cut to encircle this drum, with an allowance of overlap for joining, so as to form a complete cylinder, which should be of sufficient depth to reach from the first ring to the tower base plus an overlap of 3 in.

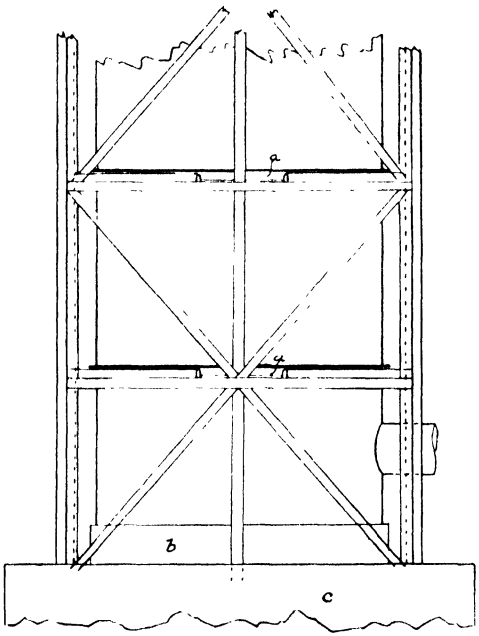


FIG. 85.

The drum and lead are now lifted into position between the tower uprights, and the upper portion of the cylinder is flashed over the first angle support *a*. The drum is then lowered, another cylinder of lead prepared, and the same process carried out until the top of the tower is reached. The second and following cylinders must, however, have an extra lap of 3 in. for flanging on to both rings. There are now only the horizontal seams to burn and the tower is ready for the packing.

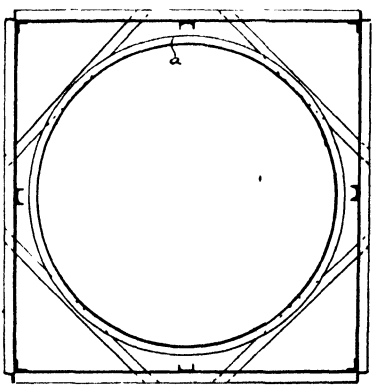


FIG. 86.

If there are more than four upright posts, one or more of them must be left out during the building of the tower, to get the leaden cylinder in.

In the south of France octagonal Gay-Lussac towers are in use, built of Volvic lava (see later on), without any lead shell.

Packing the Coke.

Coke was formerly regarded as the best for this purpose, because its irregular shape and rough surfaces offer a very large area of contact between gas and liquid. Another advantage which coke has over other materials, such as pieces of glass, earthenware, flint, etc., is its comparatively light weight. Two other advantages sometimes claimed for it, viz., porosity and resistance to chemical action, are non-existent. The contention that coke, owing to its porosity, offers a great many internal surfaces for the contact between the gas and the liquid is erroneous. In the first place, dense coke is indispensable for a coke tower; and in the second place, the pores must at once be filled with liquid, which thus cannot come into contact with the gas passing outside. It is not owing to its porosity, but to its rougher, more irregular, and therefore much larger *surface*, that coke is preferable to broken glass or earthenware, etc.

It is necessary to be very careful in the selection of the coke. Gas-coke is of no use; only the hardest-burnt oven-coke must be used, giving a clear ring, as little porous as possible, and of a silvery-white appearance. It must be carefully packed, rejecting all dull black pieces. First only the large pieces, a foot and upwards in length, are picked out. These are placed in horizontal layers directly over the grating of the tower, crossing each other if possible. Each piece must be placed by hand. In this way the first third of the tower is packed; then come the pieces next in size; and for the last third the smaller lumps may be used, and may be simply emptied in out of baskets. Nothing, however, is allowed to go into the tower which has not been sifted through a riddle with 3-in. holes. Unless a coke-tower is packed most carefully, either the draught through it will be impeded, or there will be too much free space for the gas, or, in the most frequent and worst case, the packing will be too loose in some places and too dense in others, and thus there will be bad absorption as well as bad draught.

Soft, porous coke must be rejected, for two reasons: first, it cannot support the pressure of the superposed column without being crushed, thus stopping the draught; second, soft coke is soon acted upon by nitrous vitriol, and is eventually converted into a thick paste; this is very bad for the draught, and may necessitate repacking the tower. It also imparts a dark brown, at first nearly black, colour to the acid run through the tower for a considerable time (several months) after a tower has been freshly packed.

The claim formerly made for coke, that it is not acted upon by the gases or liquids within the Gay-Lussac tower, must be declared untenable even for the hardest-burnt coke, since Lunge has shown [1] that the reason why "nitrous vitriol" never, except under totally abnormal circumstances, contains any nitric acid, even when the gases entering the tower had contained N_2O_4, is this, that the coke reduces the nitric acid originally formed from the N_2O_4 to nitrososulphuric acid. This takes place slowly at ordinary temperatures, but very quickly and completely at slightly higher ones (30° to 40°), such as generally rule in the tower.

In a subsequent investigation [2] Lunge showed that the action goes further, and that nitrous acid (*i.e.* in this case nitrososulphuric acid) is reduced by the action of coke to nitric oxide, with formation of carbon dioxide. It is true that at the ordinary, or at a slightly raised, temperature this action is only very slow; but even then it is quite perceptible, and at temperatures above 70° it becomes very strong (*cf.* p. 265, Vol. I). This no doubt accounts for some of the losses in the manufacture of sulphuric acid, and it would seem to speak in favour of employing a packing which is not acted upon by the nitre in any way. In fact, at some works the ordinary coke-towers must be repacked every few years. In places where the coke-packing has been replaced by cylinders of hard stoneware, the nitrous vitriol is very much stronger than with coke-packing under similar circumstances.

Hallwell [3] noticed a distinct saving of nitre when he replaced the coke-packing by stoneware.

[1] *J. Soc. Chem. Ind.*, 1885, p. 31.
[2] *Z. angew. Chem.*, 1890, p. 195.
[3] *Chem. Zeit.*, 1893, p. 263.

Of course, dense coke is less acted upon than porous coke—the latter does not even resist the action of pure concentrated sulphuric acid without disintegration; but in the end all coke is gradually wasted, and long before this is done to such an extent that the real loss of weight would make it necessary to replenish the tower, the mud formed by the disintegration of part of the coke stops up the draught to an intolerable extent. Flushing the tower with water is sometimes a remedy, but is far from being always efficacious.

In the case of very high towers, sometimes one or two grids are interposed at various heights for supporting the upper layers of the coke. These grids are made of iron bars cased in lead. Unless they are very carefully arranged, they may go down with the coke packing as the latter gradually sinks, and may do more harm than good.

The drawbacks existing in the case of coke-packed Gay-Lussac towers have long since led to the employment of other kinds of packing.[1]

In the *Alkali Report* No. 52 of 1915, a list is given of the packings of 440 Gay-Lussac towers in the United Kingdom:

Description of packing	Balls.	Bricks.	Coke.	Glass.	Lunge-Rohrmann tiles.	Rings.	Tiles.	Bricks and tiles.	Rings and coke.	Rings and tiles.	Bricks or tiles and coke.	Total.
Number of towers.	1	53	269	48	3	25	17	10	8	4	7	440
Per 1000 towers .	2	120	611	98	7	57	39	23	18	9	16	1000

A complete design of a coke-packed Gay-Lussac, with illustrations, is given in Lunge's fourth edition, p. 796.

The tower stands on strong brick pillars with an arched top. Above this follows a hollow network of acid-proof brickwork, serving as cooling-channels for the wooden floor, the outside of which is provided with the circular lead spout to prevent any acid running over on to the foundations. Six wooden pillars form the uprights for the leaden shell of the tower; they are tied at top and bottom by cross pieces, forming a hexagonal frame. Cast-iron brackets fixed in the uprights support the

[1] For full details of various kinds of packing see end of this chapter.

lead sides of the tower, keeping these at a distance of 1 in. away from the wood.

The bottom of the tower is formed of a lead dish, 6 in. high; this is made of lead 14 lb. to the square foot. The sides and top are made of lead 7 lb. to the square foot. The inside of the tower is lined at the bottom up to the top of the grate with 13-in. brickwork, above that 7 ft. high with 9-in. brickwork, above that 12 ft. high with 4½-in. brickwork; the remainder of the shell up to the top has no lining.

The lead bottom is protected by thin acid-proof slabs. On these are erected pillars, which carry stoneware grids, each consisting of three pieces, supported by the recesses of the pillars. These bearers are 5 in. wide, 16 in. high, and leave open spaces between them, 7 in. wide. They are bridged over by bricks, which support the packing, formed of cylinders, to a height of 7 ft. The cylinders (about which *cf.* end of this chapter) are placed so that each of them stands on the crossing-point of four other cylinders. On the top of this packing there is a lead-covered cast-iron grid, upon this 12 ft. high of coke-packing, then another grid, and again nearly 12 ft. coke-packing. The top is formed by a shallow lead dish of 12 lb. lead 2 in. deep, with a number of acid "lutes."

This tower is 9 ft. 4 in. wide and 41 ft. high within the lead; the inlet and outlet pipes are each 25½ in. wide.

Falding[1] gives a design of a Gay-Lussac tower which does not essentially differ from the above.

Both the inlet and outlet pipes of the Gay-Lussac should be provided with a contrivance for *the observation of the colour of the gas* before and after its passage through the tower—for example, two glass panes placed opposite to each other; or a portion of each of the two pipes may be made of glass. It is a very good plan to make the "sight" in the shape of a narrow lead box, 6 or 7 ft. long, with glass panes at the opposite small ends. In this case the colour is seen through a deep layer of gas, and any admixture of yellow vapours is much more easily discovered than with the ordinary small sights.

Plate-towers (*Lunge towers*).—An exceedingly suitable apparatus for this purpose is the plate-tower, mentioned on p. 69 *et seq.* Lüty[2] gives reports from eleven different

[1] *Min. Ind.*, 7, 691. [2] *Z. angew. Chem.*, 1897, p. 485.

firms in Germany, Austria, England, America, and Russia, which had erected plate-columns as Gay-Lussac towers, and were perfectly satisfied with the results. Niedenführ[1] quotes reports from factories, showing that the loss of draught with plate-towers is much less than with coke-towers (only 1·5 mm.), and that the former, if combined with the latter, consume less nitre and produce more acid than coke-towers alone, especially by the equalisation of disturbances in the work.

A very good plan, where several sets of chambers are at work in the same factory, is to provide each set with a first Gay-Lussac tower in the shape of a "Lunge tower" and to convey the gases from all these into a large central coke-tower. The large quantity of weak nitrous vitriol employed in the latter is then employed for feeding all the plate-tower Gay-Lussacs of the individual sets (*cf.* p. 169, the Griesheim system of centralising the Gay-Lussac towers). In this case, the action on the coke is negligible, owing to the low temperature and the slight amount of nitre to be dealt with in the central coke-tower.

A Lunge tower of 15 or 20 ft. is said to do the same work as a much wider coke-tower of 30 or 40 ft., and causes only a quarter or a sixth of the loss of draught produced by the coke-tower (Niedenfuhr, 1902).

The combination of plate-towers and a large central coke-tower has the further advantage that any inequalities of work are thus rendered practically harmless, and the only real objection to plate-towers, viz., the small stock of acid which they contain, is thus completely avoided. As these towers are so low, it will be possible in most cases to place their tops at a slightly lower level than the bottom of the coke-tower and to feed them directly with the acid running from the latter without the necessity of again pumping up the weak nitrous vitriol.

Some of the towers packed with bricks or cylinders have not answered their purpose because the packing was too loose and not nearly so efficient for surface contact as coke-packing; but experience has now shown that the latter, the chemical drawbacks of which have been pointed out before, can be replaced by chemically resistant stoneware, if moulded into

[1] *Chem. Zeit.*, 1897, p. 20.

proper shape, and that in this way the tower can be made very much smaller than coke-towers, say one-sixth to one-tenth or even less.

Repacking Gay-Lussac Towers.—Coke-towers, owing to the circumstances described above, must be emptied and repacked from time to time. This must be done with great care, on account of the nitrous gas present in the towers, which is very poisonous. The precautions to be taken in emptying Gay-Lussac towers are mentioned in the *Thirty-Third Annual Report of the Inspector of Alkali Works* (for the year 1896), and in the *Forty-Third Report* (for 1906). The *Forty-Ninth Report* (for 1912), p. 12, enumerates the precautions which should be taken in this operation:

(1) Washing the tower with strong sulphuric acid, to remove any nitrous vitriol, prior to washing with water and steaming.

(2) The maintenance of a downward draught, to remove as directly as possible any gases present from the men engaged at the work.

(3) The use of a "safety pipe," as required by the Special Rules of the United Alkali Co., Ltd. This safety pipe consists of a metal funnel, the stem of which acts as inlet-pipe. It fits with a pneumatic pad against the face (this pad can readily be blown up for use, being similar to that used in dentistry in the administration of nitrous oxide), and is fastened on by a strap buckling behind the head. The safety-pipe case contains 50 ft. of pipe, and is used by men engaged in cleaning out vitriol chambers, Gay-Lussac towers, etc.

Respirators for men dealing with dangerous gases are described and illustrated in *Chem. Ind.*, No. 14, Beilage, pp. 30 and 31.

Schubert[1] points out the frequency and dangerous character of poisoning by nitrous vapours, the effects of which often only appear several hours after breathing the gas. He recommends a series of precautionary measures to be taken at the factories, and the use of dilute liquid ammonia for moistening pieces of cloth to be kept in front of the mouth and nose.

[1] *Chem. Zeit. Rep.*, 1912, p. 26.

In the *53rd Alkali Report* (for 1916) a description is given of an experiment made at a Swansea works. The Gay-Lussac tower, which contained coke packing, was washed with acid and then with water, the washing being continued for four days, until the wash water was free from acid. The nitrous fumes evolved whilst washing with water were led to the Glover tower and another set of chambers, whereby potting was saved for two days and the acidity of the exit was reduced to 0·5 grains SO_3 per cub. ft. The washing resulted in the coke falling out in loose pieces, thus avoiding the breaking-up process necessary after long service in a coke-packed Gay-Lussac tower. Washing for ninety-six hours may not be necessary in every case, and when the nitrous gases can be utilised the preliminary washing with acid can be omitted.

Chloroform has been found to be very efficient as an *antidote* against poisoning with nitrous vapours.[1] The following rules for its application have been issued by the Rheinisch-Westfälische Sprengstoff Company. The person afflicted is to take 3 to 5 drops of chloroform, poured out of a drop-flask into a tumbler of water, once every ten minutes. The drop-flasks hold 0·5 gram chloroform, which is the maximum dose allowed by the German Pharmacopœia for a single taking; 1·5 gram or the contents of 3 drop-flasks is the maximum for a day. The weight of 3 drops chloroform is 0·045 gram; that of 5 drops, 0·078 gram. According to Reusch,[2] strong and long inhalations of *oxygen* are preferable to the chloroform treatment.

Special rules have been officially laid down in Germany for repacking Gay-Lussac and Glover towers.[3]

The *Chem. Trade J.* supplies posters for fixing up at chemical works, containing *Rules for Dealing with Dangerous Gases*, of which the following is an abridged abstract:—

No person may enter a boiler, tank, drain, vitriol-chamber, or tower, unless provided with a suitable respirator in good condition. If the gases cannot be absorbed, the men must be provided with a face-piece supplied with air or oxygen. They must be secured round the waist by a rope, and a man must be

[1] *Chem. Ind.*, 1904, pp. 296 and 379.
[2] *Chem. Zeit.*, 1911, p. 289.
[3] *Chem. Ind.*, 1897, p. 365.

in attendance to render assistance if necessary. If a man is "gassed," he must be speedily removed into the open air, or placed in a warm, well-ventilated place. In bad cases an oxygen bottle (never to be used without a reducing-valve!) and lung exercise must be employed. If the man is conscious, the valve is very slightly turned on and the oxygen introduced into his mouth by a glass tube. If unconscious, the tube is put in one corner of the mouth, the lips are closed round it, and artificial respiration is produced in the usual way. If the teeth are set, put the tube in one of the nostrils. The "lung exercise" (described in detail in the "poster") is the same as that used in cases of drowning, and is not often necessary.

Other Nitre Recovery Apparatus.—Instead of the Gay-Lussac tower, various other arrangements have been proposed from time to time, and Lunge in his first edition, pp. 377-378, and in his fourth edition, p. 797, describes several appliances, but they appear to offer little advantage over the ordinary column.

Fulda (U.S. P. 1084953) regenerates the nitric acid in a series of chambers, containing from 20 to 30 or 50 per cent. of the total volume of the chambers, in which the nitrogen oxides are successively exposed to contact with acids of sp. gr. 1·21 to 1·26; 1·07 to 1·21; and 1·00 to 1·10.

Moritz (Fr. P. 462877) provides absorbing- or reaction-towers with vertical or horizontal partitions, so that the liquid can run down freely, but the gases must take a circuitous route. The partitions are kept in their places by the packing.

Höfling (Ger. P. 272608) arranges the packing within the towers after the manner of a winding staircase, whereby the gases are compelled to overcome a great friction and mixing resistance, and also, in their spiral passage, to separate the liquid particles. If the acid is run down from the top and heating gases are passed in below, the tower may act as an acid-concentrator. According to his Ger. P. 281135, he employs pieces of tubing, provided with holes and diaphragms, built up in the towers in such a way that through-going channels are avoided.

The application of silica gel for use in recovery of the oxides of nitrogen has been attracting considerable attention, and a great deal of work has been done in this direction in

Canada. There are, however, no very definite data nor apparatus obtainable at the moment for working on a commercial scale.

Distribution of the Acid Feed.

It is of great importance, for the working of Gay-Lussac towers (as well as of Glover towers, etc.), that the supply of sulphuric acid, which is to deprive the gases of their nitrous acid, be exactly regulated, and that from the beginning this acid be spread equally over the packing. Otherwise too much sulphuric acid is used, and yet the gas may pass through the tower without giving up the whole of its nitrous oxides. Special care must be taken, therefore, in the construction of the apparatus for spreading the acid. At one time this was performed by a number of small taps which evidently could not be regulated for a very slight flow without danger of being stopped up; or by "tumbling boxes" and the like.

In England the acid-distributor is usually made of lead. Descriptions of the spreading-wheels are given in Lunge's first edition, pp. 438 to 440, and in the second edition, pp. 587 and 588. Reaction-wheels are described in the fourth edition, p. 799.

Even the best-constructed acid-wheels are liable to get stopped now and then, and this sometimes causes a great deal of trouble if it is not at once perceived, as the tower then ceases to work properly and a great amount of nitre gets lost. A new system has been introduced, which works quite as well as the acid-wheels and has no mechanical movement liable to be disturbed. It consists in running the acid into a vessel provided with a number of *overflows* kept exactly at the same level, each of these communicating with a separate pipe which leads the acid into the tower. This system can be carried out in a variety of ways, one of the best of which is shown in plan in Fig. 87, in transverse section in Fig. 88, and in perspective view, with the sides partly cut away, in Fig. 89. From the tap *a* the liquid runs into the central vessel A. The cover *b* is not absolutely necessary, but is best provided, and is made loose, so that the interior of A is easily accessible. The cylinder A is nicked at the bottom, so that it communicates with the wider but lower trough B. This is provided all round

its circumference with overflow-lips *c c*, which may be close to one another; sometimes 30 or 40 of these are made. They must be arranged in such a way that when B is once filled, all

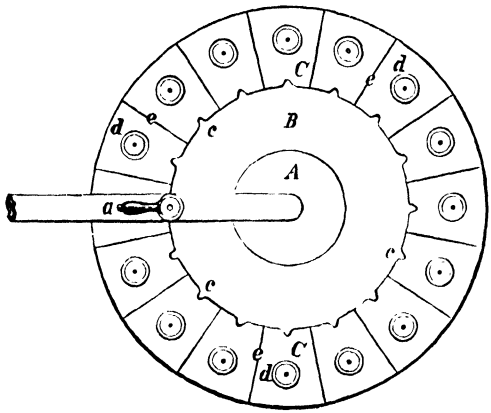


FIG. 87.

the overflows *c c* function precisely alike. This can easily be attained by dressing the lead of the lips a little up or down, as the case may require. Once right, they always act in the same

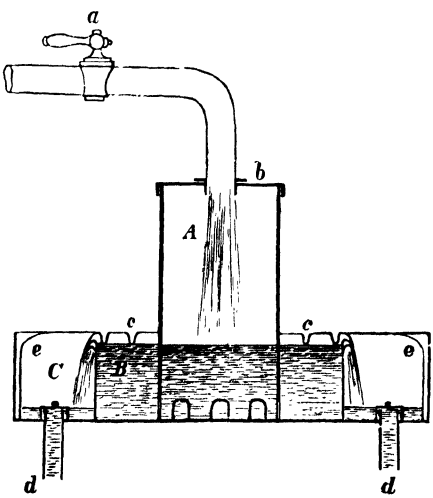


FIG. 88.

manner. The trough B is surrounded by the wider trough C, which is divided into as many cells as there are lips in B. Each cell is independent of its neighbour, but the partitions,

e e, are cut out on the top, so that in case of the pipe of any one cell getting stopped up the liquid overflows into the next cells. Each cell is also provided with a separate pipe *d*, made tight in the bottom of the cell, and hydraulically sealed either there, as it is shown in the diagram, or else on or within the tower. The whole is generally, in the case of Gay-Lussac towers always, made of lead, but it may also be made of earthenware, or other suitable material.

Briegleb (Ger. P. 10386) has constructed a distributing-

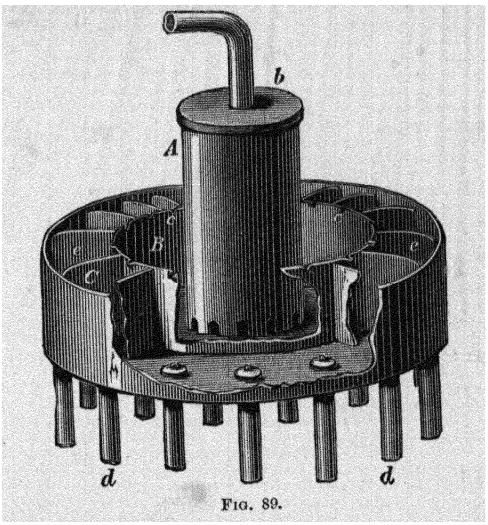


FIG. 89.

apparatus consisting of a cone made of regulus metal, on the top of which a jet of acid is directed. The upper part of the surface of the cone is plain, but the lower part is fluted, so that the acid is distributed into a number of jets which are caught in a circular vessel surrounding the base of the cone, and are carried away separately by pipes. No doubt this apparatus can be made to work properly, but it is much less easily kept in order than the simple overflow apparatus shown on p. 160.

In the case of towers of great horizontal section, where the number of pipes coming from the distributor is inconveniently large, a great deal may be saved by employing only one pipe to every four holes on the top of the tower, each pipe ending over a small trough placed at the point of intersection of the lines connecting these four holes. These small troughs will

then empty their contents simultaneously into all the four holes. Of course, the same precautions have to be taken for securing an equal flow into all the four holes as mentioned in connection with Figs. 87 to 89.

Hommel and the Metals Extraction Corporation (B. P. 19668 of 1908) describe a special form of the apparatus for dividing the acid in Gay-Lussac or Glover towers.

Klute and Ising (Ger. P. 209276) place between the acid-tank and the distributing apparatus a float-valve provided with several outlet pipes, which can be shut off separately, so that, in case of altering the supply of acid, each pipe is opened entirely and cannot be stopped up by foreign bodies, which easily takes place in the case of partially opened valves.

The action of a column (whether it be a Gay-Lussac, or a Glover tower) is, of course, all the more efficient the more uniformly the feeding-acid is distributed over its whole area. It is equally obvious that towers of a large horizontal section require more feeding-places than narrow ones. It may be laid down as a general rule that there ought to be no smaller number of distributing-pipes than one to each superficial foot of the cover of the tower; but this is a minimum which is greatly, and no doubt advantageously, exceeded at many works.

Another way of dividing the feeding-liquids for absorbing, condensing, and reaction-towers is described by the Farbenfabriken vorm. Fr. Bayer & Co. (Ger. P. 241767). They employ layers of a porous material, like sand, powdered coal or metals, or plates, rods, small tubes, etc., of a porous material, like burnt clay, sintered quartz, porous cement, etc., through which the liquid percolates, and is made to drop off at suitably arranged edges or points. By changing the grain, the porosity and the thickness of the porous layer, as well as the height of liquid on the dividing plates, the velocity of feeding can be regulated at will.

The *regularity of the supply of acid* to the Gay-Lussac tower is of the utmost importance for its good working. The whole acid-chamber process is so constituted that its course must be kept as continuous and uniform as possible, and the large volume of the lead-chambers in this case serves as a regulator, similar to the air-vessel of a blowing-engine, so that the gas, on leaving the chamber, issues, or at least ought to issue, with

absolutely uniform speed and composition. In equal intervals of time there will therefore be equal quantities of nitre-gas leaving the chambers, and these should always find the same quantity of acid in the absorbing-tower; if not, there will be either an escape of nitre-gas or the nitrous acid will come out too weak. If the acid flows out of a tank and the tap is always left open to the same extent, the flow will be much quicker at the beginning, when the tank is full, than afterwards, when it is partly empty, and the tower will thus be fed very irregularly. The speed of outflow of liquids is proportional to the square roots of the heights of liquid in the tank; for instance, when the tank is filled to the height of 4 ft., the flow of acid will be twice as fast as when it only stands 1 ft. high.

Lunge in his fourth edition, pp. 826-828, describes a balancing apparatus consisting of a lead cylinder of equal height to the adjoining store tank, with which it is connected at its lowest point. The connection contains a valve-seat into which a ball is suspended from a rocking beam fixed above the tank. At the opposite end of the beam a float is attached which moves in the cylinder according to the depth of acid in the tank, and is adjusted so as to maintain a pre-determined level in the cylinder.

Fig. 90 shows a useful type of *acid valve* which is resistant to all chemical action and will withstand severe alterations of temperature. It is supplied by the Universal Valve and Chemical Co., Dudley Hill, Bradford, who claim the following advantages:

The flanges of the valve body may be set at any angle desired from right angles to parallel without in any way affecting the free working of the valve, thus making it exceptionally adaptable. The valve-seat is provided with two working faces. Should one face wear the seat may be reversed, and a new face presented to the valve. When both faces become worn a new seat can be quickly substituted. The method of securing the seat is such that it cannot come loose under working conditions. The fixture of the valve to the spindle is so designed that, whilst providing sufficient flexibility to ensure perfect seating, it cannot come off the spindle under working conditions. The valve-plug is of the non-rotative type and is easily renewed when necessary. The

valve-seat and plug are made of special non-absorbent vitreous pottery, as resistant to the action of all chemicals as Berlin porcelain, with remarkable heat-resisting properties. It has a compression strength of 24 tons per square inch and a high tensile strength. The body of the valve and valve-spindle are made in any metal or alloy to suit special conditions or chemicals it is desired to handle. A special feature is made

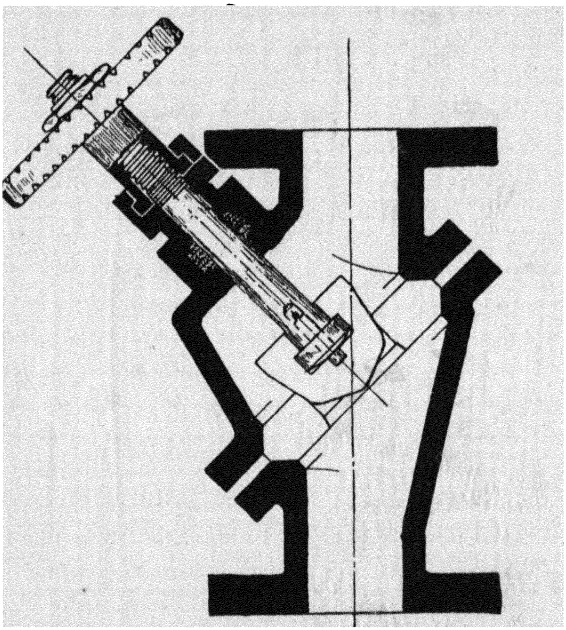


FIG. 90.

of standardization and interchangeability, guaranteeing the fit of any spare parts ordered for replacement.

J. Cortin, Ltd., Newcastle-upon-Tyne, and Appleton & Howard, St. Helens, make *non-rotative acid valves* of a special mixture of regulus metal, the plug rising or falling into its seat out of a fixed setting without turning round, so that it is free from friction in working, and the wear and tear are reduced to a minimum.

A. M. Fairlie [1] describes several types of valves. The Ceco valve developed at the Victor Chemical Works, Chicago Heights, Ill., is of interest. In designing this valve, the

[1] *Chem. and Met. Eng.*, **25** (1922), p. 969 *et seq.*

features aimed at were: (1) A removable seat which could be withdrawn without disconnecting the entire valve and which could not corrode in place. (2) A seat which would not accumulate scale. (3) Flexibility as to angle of installation. (4) Operating mechanism inaccessible to acid or acid fumes. (5) A packing gland without studs.

The removable seat is made of a flat slab of metal held in place between two flanged faces on the valve body. The seat is identical as to shape on both sides, thus making it reversible, and it can be removed without disconnecting the valve from the pipe-line. Only a few minutes are required to reverse or replace a seat.

In the ordinary valve, a tapered plug fits into a tapered seat, and any accumulation of scale or sediment on either plug or seat prevents effective closing of the valve. In the Ceco valve, the hole within the slab-seat is cylindrical, and on a new valve the seating edge is quite sharp. Even after a valve has seen considerable service, the manufacturers claim, the seating is virtually a line contact. This means a minimum of area for the deposit of scale or sediment, and if scale does form on either of the seating members, it is said that the act of closing the valve tends to break away the scale. To prevent sticking of the plug, a relieving taper is provided thereon. A taper is machined also on the upper side of the plug, and at the top of the valve body another seat is machined, so that when the valve is wide open, the upper part of the plug is again seated on a line contact, the object being to seal the stuffing-box against leakage, and permit the repacking of the valve while under pressure.

In order to broaden the scope of application of this valve to service, the body of the valve is divided into two parts at an angle of 45 degrees. This permits of assembling any valve in either a straight or an angle position. Thus, using the same valve parts, the straight-way valve can be changed into a right-angle valve by turning that part which is on the left of the removable seat 180 degrees, so that the valve stem and handle are below the left-hand flange, instead of above it.

A section and plan of a float valve of the packingless type manufactured by the Chemical Pump and Valve Co. are shown

in Figs. 90*a* and 90*b*. The valve is provided with a flexible diaphragm which walls off the acid from the bearing of the valve stem. There is consequently no need of a stuffing-box or packing. The flexible diaphragm is of lead, if the valve is to be used with sulphuric acid. The manufacturers state that

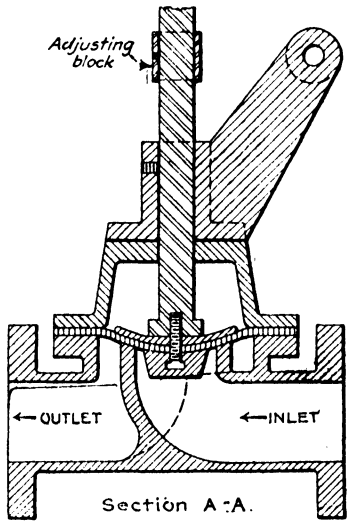


Fig. 90*a*.

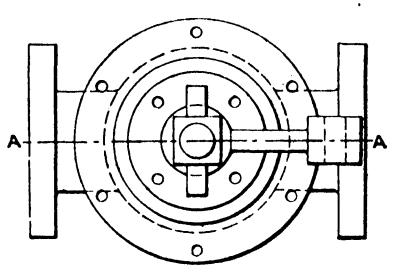


Fig. 90*b*.

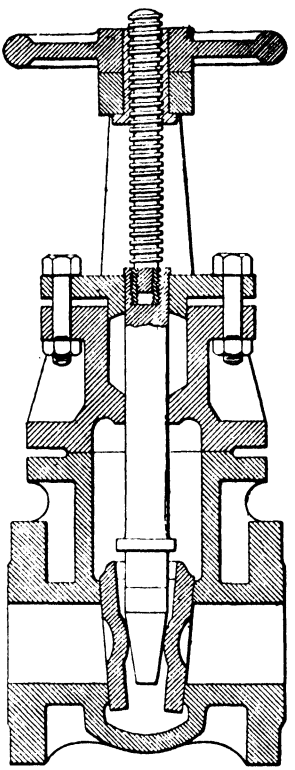


Fig. 90*c*.

owing to the limited movement of the diaphragm, the valve may be opened many hundreds of times before the lead cracks. When the lead does crack, it becomes necessary to drain the line, open the valve and put in a new diaphragm. It should be noted that owing to the design of the valve, the line cannot be drained unless the valve, when installed, is placed on its side. This valve is made in all sizes from 1 in. to 18 in., the capacity of the latter being 5000 gal. per minute.

Fig. 90*c* shows a section of a Duriron gate valve which was first put on the market in June 1920. It is a valve of the rising stem type. As the metal is highly resistant to corrosion it is claimed that this valve will not stick under the most trying conditions. Gate valves of the ordinary type are inefficient as a positive shut-off for acid, particularly if the acid handled contains solids in suspension. This valve has double-hinged discs which the manufacturers claim afford positive closure on both seats, and the valve can be used against pressure from either direction. The wedge action of the stem eliminates any wear and tear on the discs or seats,

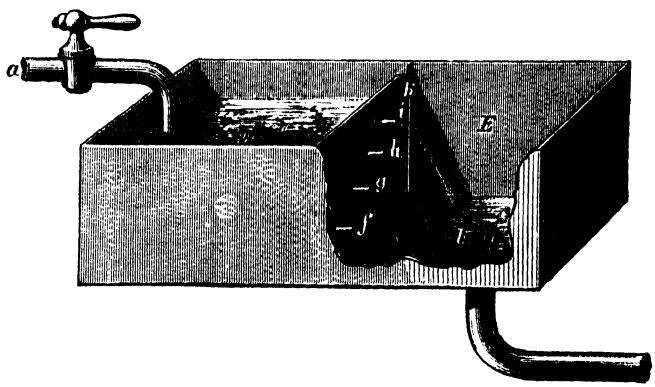


FIG. 91.

and the valve is so positive in its action that it is said to be useful with gases as well as liquids. The valve can be packed whilst under pressure.

For regulating the rate of feeding, some works employ the contrivance shown in Fig. 91, which is interposed between tap *a* and the central vessel A in the apparatus, Fig. 89. The liquid runs from *a* into a leaden box, divided into two compartments, D and E. D communicates with E by the four pipes, *f*, *g*, *h*, *i*, placed at different levels, and the lip *k*. E is provided at the bottom with a wide outlet-tube *l*. According to the amount to which tap *a* is opened, box D will be more or less filled ; with the strongest feed, the acid will run into compartment E out of all four pipes and the lip *k* ; with a smaller feed, fewer of the pipes will come into action. Supposing the attendant is instructed to work with three pipes, he will have to see that the acid runs out of *f*, *g*, and *h* only,

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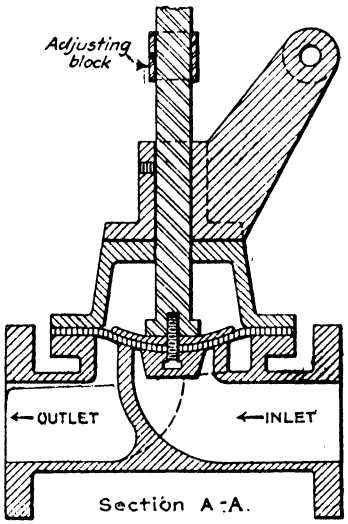

FIG. 90*a*.

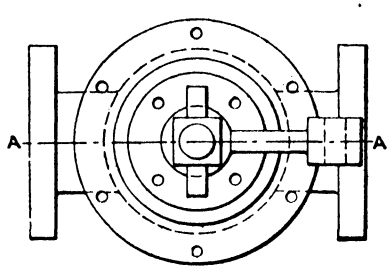

FIG. 90*b*.

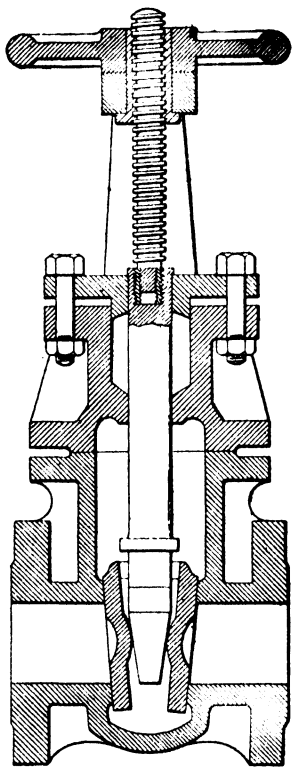

FIG. 90*c*.

owing to the limited movement of the diaphragm, the valve may be opened many hundreds of times before the lead cracks. When the lead does crack, it becomes necessary to drain the line, open the valve and put in a new diaphragm. It should be noted that owing to the design of the valve, the line cannot be drained unless the valve, when installed, is placed on its side. This valve is made in all sizes from 1 in. to 18 in., the capacity of the latter being 5000 gal. per minute.

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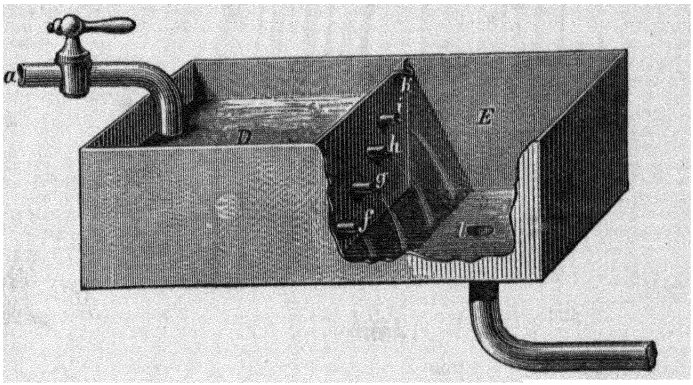

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the pressure being almost constant at the level of *h*. This, of course, is greatly preferable to regulating the position of tap *a* by mere rule of thumb, and it operates independently of the level of acid in the main reservoir to which tap *a* belongs. This contrivance acts very well.

Pauling (Ger. P. 242515) employs a reservoir connected on one side with a filling apparatus acting from time to time, on the other side with an apparatus which divides the liquid into a series of jets.

William Mason[1] describes an overflow distributor of the type of a spinning-wheel, and a new form of outside and inside coolers.

Noll (Ger. P. 276665) describes an apparatus for mixing liquids with gases, consisting of a ring tube with outlets for the liquid surrounding the gas-pipe which enters into the cylindrical mixing pipe.

Briggs (U.S. P. 1032657, assigned to the General Chemical Company) employs a conical distributor, fluted outside, below which is a perforated disc, the holes in which correspond to the outlets of the distributor.

Fowler and Medley (B. P. 23864 of 1911) cause the liquid to run from the outside to the centre, where it is atomised by quickly revolving discs.

Rabe (Ger. P. 284857) describes an arrangement for wetting surfaces of any form by means of periodically formed liquid bells of changing diameter, dissolving into drop-like rings. For producing these, a circular plate is provided, with a turned-up edge, which at its bottom gradually contracts to a rod, down which the liquid contained in the plate runs freely, influencing the diameter of the liquid bell solely by its quantity. The periodical change of the quantity of liquid is produced by a siphon, the descending branch of which is connected with a closed vessel containing outlets with the same resistance for the single branch conduits, which may be arranged in groups. The periodical siphoning automatically fills all the branch conduits, as they have all the same resistance, and washes away the impurities remaining at the conclusion of the siphoning and during the retardation of the current at the next siphoning, so that no special supervision is required.

[1] *Chem. Zeit.*, 1914, p. 800.

Centralised working of the Gay-Lussac Towers.—The following system is followed at the Griesheim works. Seven sets of chambers are employed, each possessing ordinary Gay-Lussac towers. The whole of these communicate with a large common tower, of a horizontal section of 10 × 30 ft., which receives the fresh acid of 142° Tw., divided into 480 jets. The resistance in this tower amounts to $\frac{1}{12}$ up to $\frac{1}{8}$ in. of water. The weak nitrous vitriol formed here is pumped up and feeds the ordinary Gay-Lussac towers. Since these require variable quantities of acid, this is divided among the seven towers by an acid-wheel having seven chambers of variable dimensions, formed by slightly inclined movable spouts resting on the partitions between the chambers. By shifting these spouts backwards or forwards, the time of feed and also the quantity of acid serving each compartment can be varied at will. A pipe conducts the acid from each compartment to one of the Gay-Lussac towers, where it is again subdivided in the ordinary way. (In the same works there is a similar arrangement for dividing the strong nitrous acid, chamber-acid, and nitric acid among the seven Glover towers, placed at a considerable distance from the central office.) Figs. 92 to 95 illustrate the above. Fig. 92 shows the acid-wheel, supported by the glass bulb *a*, floating in a vessel filled with sulphuric acid. This avoids all friction, so that the wheel never stops. The glass point β and a short piece of tubing at the bottom form one of the guides; a thimble δ, just below the funnel, constitutes the other guide. The seven compartments, *a*, *b*, *c*, *d*, *e*, *f*, *g*, and the spouts γ (Fig. 95), can be moved backwards and forwards, and thus admit of dividing the supply at will. Thus, for instance, in Fig. 95, which represents a section through all the seven compartments (projected on a straight line), the acid is divided among the six compartments, *a*, *b*, *c*, *e*, *f*, *g* in the proportion 7, 7, 7, 8, 5, 8; *d* receives nothing, because the set of chambers to which it belongs is out of use.

At Griesheim the nitrous vitriol is thus brought up to a strength equal to 60 grams $NaNO_3$ per litre, and the total consumption of nitre has been brought down to 0·83 per 100 H_2SO_4. This system allows of keeping one of the sets with an excess of SO_2, since such excess is counteracted by the

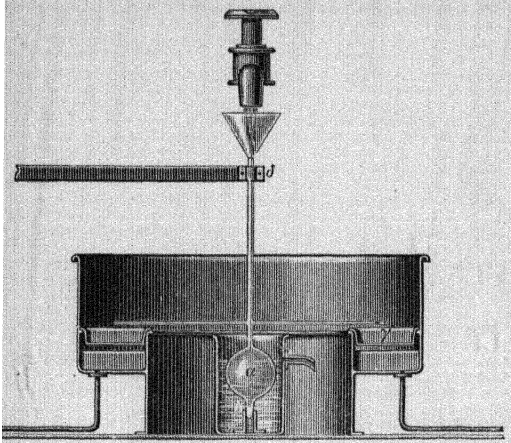

FIG. 92.

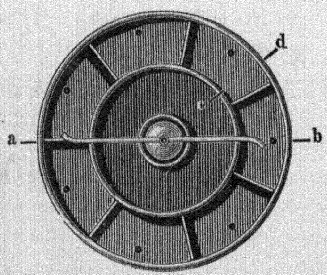

FIG. 93.

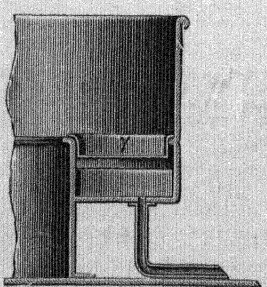

FIG. 94.

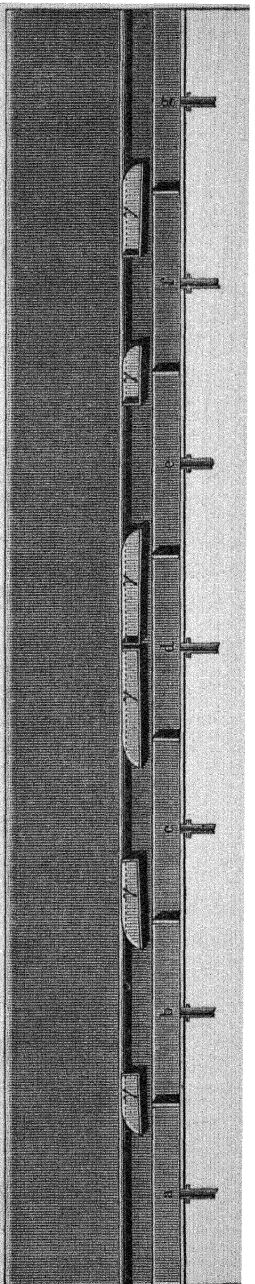

FIG. 95.

nitre contents of the gases from the other sets in the central tower.

Pumping Apparatus for Acid.

To feed the acid tank on the top of the absorbing or other tower, an apparatus is needed to force the acid to the top.

Acid-Eggs.—The ordinary plan of working (introduced about 1838 by Harrison Blair) is to convey compressed air into the pressure-apparatus, above the surface of the acid. In this proceeding there is no special limit of height, so long as the apparatus is made strong enough to resist the pressure, and the air-compressor is sufficiently powerful.

The vessel serving as pressure-apparatus is made in cast-iron. It is now generally made as shown in Fig. 96. Experience has everywhere shown that it is needless to protect the cast-iron of the acid-egg by a lining of lead; even the nitrous vitriol and the chamber-acid act so little on cast-iron that such a protection becomes unnecessary. Lining with lead has this drawback, that as soon as a little air gets between the lead and the cast-iron through the smallest possible chink the lead is driven away from the iron in many places, and its protecting action becomes quite illusory, whilst the contents of the egg are diminished. *Dilute* acids are best pumped up by means of stoneware acid-eggs, as supplied by Doulton & Co., Ltd., Lambeth, or by stoneware pulsometers.

The horizontal form has several advantages over the vertical:—first, that no well is needed for the acid-egg, which may lie on the floor and thus is accessible all round; second, that in the case of excessive pressure, the weakest part (viz. the manhole) being situated sideways, the acid squirting out is not so likely to injure men and machinery as in the case of squirting out vertically, especially if the cylinder is placed with the manhole turned away from the machinery.

In Fig. 96, A is the acid-egg the walls of which are at least 2 in. thick; *b* is the neck, with the manhole lid *a* fixed to it by bolts and nuts; a thick washer of india-rubber or composition-lead piping makes the joint tight; *c* is a recess at the bottom of A, into which the delivery-pipe *g* projects, in order to expel the contents of A as completely as possible; *d*, *e*, and *f* are

three branch-pipes—*d* for introducing the acid, *e* for the air-pipe, and *f* for the delivery-pipe. Each pipe has a strong lead

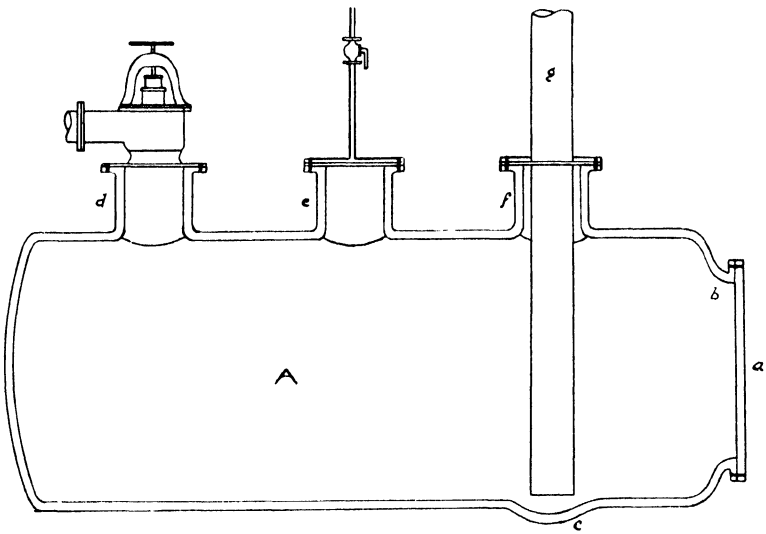

FIG. 96.

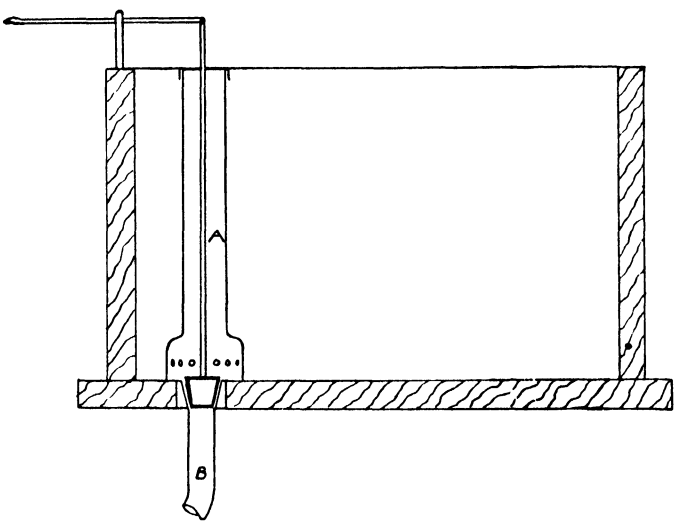

FIG. 97.

flange burnt to it, which rests on the flanges of the branches, *d*, *e*, *f*; by putting loose iron washers on the top, and screwing all

three together by bolts and nuts, the joint becomes perfectly tight. The branch *d* has an inlet-valve for the acid, and is connected with B, the outlet-pipe of the acid-supply tank, Fig. 97. The large diameter pipe A (Fig. 97), over the plug and seating, is for preventing the acid from being splashed over should the air-pressure pass through the valve inadvertently. A contrivance is adopted to avoid splashes of acid falling about

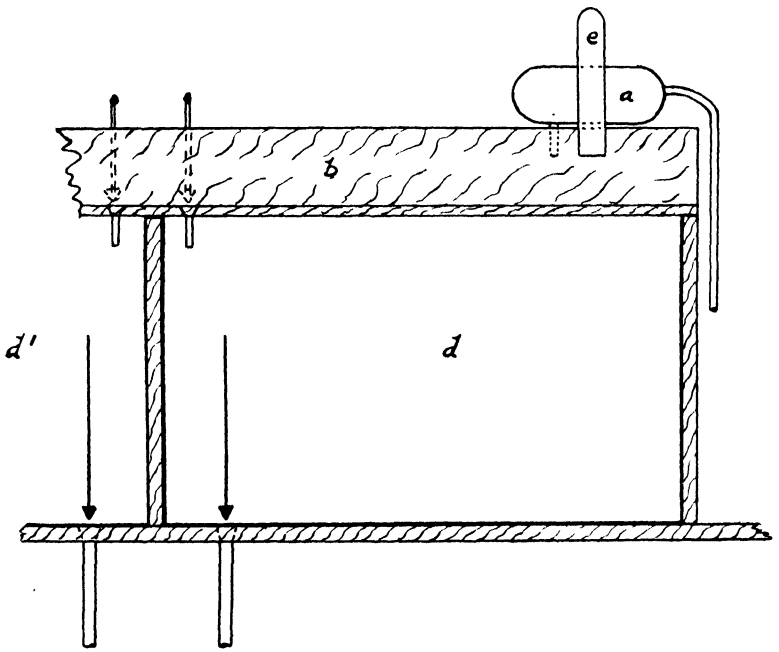

FIG. 98.

the tower-house when the acid arrives at the top of the tower. This device is especially useful when the acid-egg is just emptying. It is illustrated in Fig. 98. The cylinder *a* is made of 20 lb. lead, or of acid-resisting iron, and must be well supported above the level of the distributing trough *b*, in which are placed regulus plugs and seatings for the purpose of conveying the acid into the respective store-tank *d*, *d'*. The trunk *e* is provided in the top of the cylinder to convey splashes of acid into the store.

In smaller works there is usually only one acid-egg, which serves for pumping all the strong acid, nitrous vitriol, and

chamber-acid, one after the other; but it is very advisable to have at least two acid-eggs, of which one usually serves for the strong acid and nitrous vitriol, the other for the chamber-acid.

Pulsometers.—A somewhat different kind of acid-lifting apparatus is Laurent's pulsometer. It is made of cast-iron

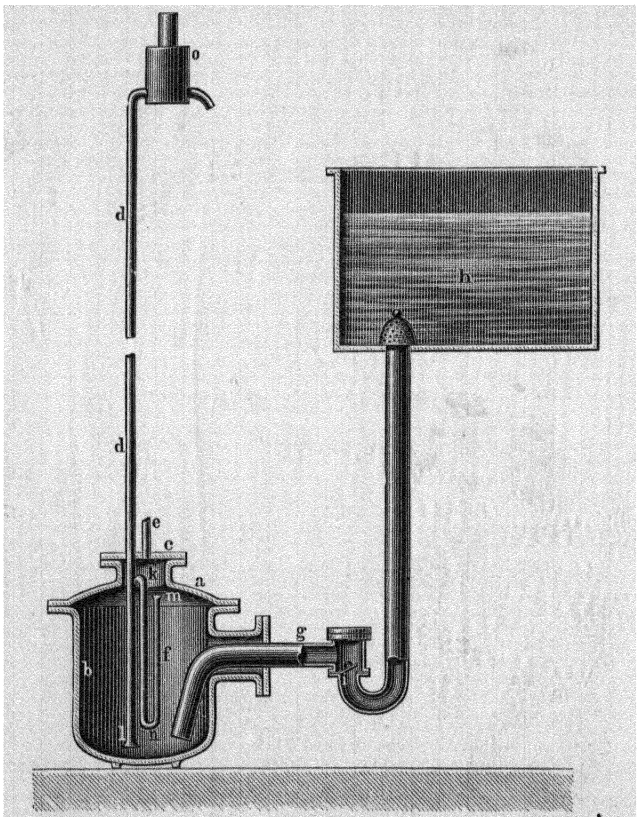

Fig. 99.

with lead pipes for sulphuric acid (Figs. 99 and 100), and of stoneware for nitric acid (Fig. 101). In the former case the joint between the cover *a* and pan *b* is best made good by a lead washer, in the latter case by an india-rubber washer; *c* is the manhole, with the rising-main *d* and the pipe *e* for compressed air. The rising-main *d* has a side connection with the swan-neck pipe *f*. The feed-pipe *g* is connected with the store-tank *h*. The latter must be fixed at

such a height that even when the pulsometer is quite full, and *h* nearly empty, there is still a greater head of liquid on the pulsometer than the length of pipe *f*. The clack *i* (which may be replaced by a ball-valve or by a Bunsen valve, as shown in Fig. 99) prevents the acid from being driven back into *h* whilst rising in *d*. Pipe *d* must be fixed in such a manner that it can be taken out together with pipe *f*, in order to attend to the latter.

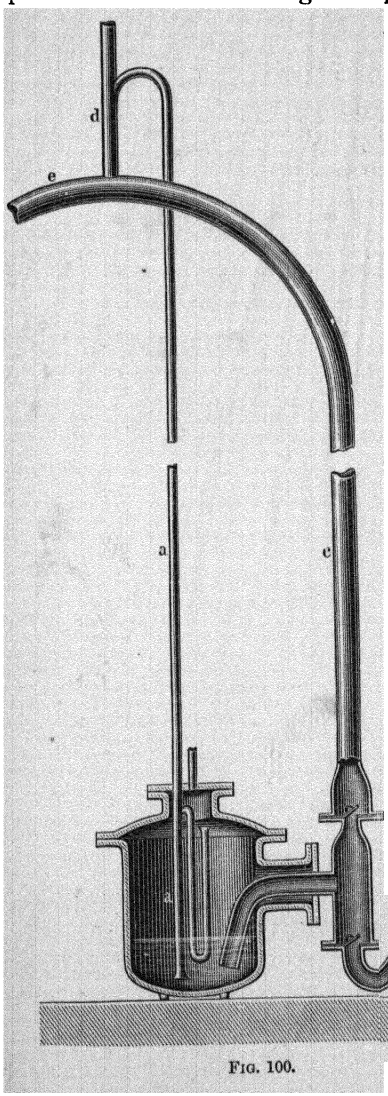

FIG. 100.

The working of the apparatus is fully described in Lunge, 4th ed., p. 822 *et seq.*

It is possible to lift liquids to a greater height than corresponds to the available pressure of air, by placing a second pulsometer midway up the height to be overcome, and

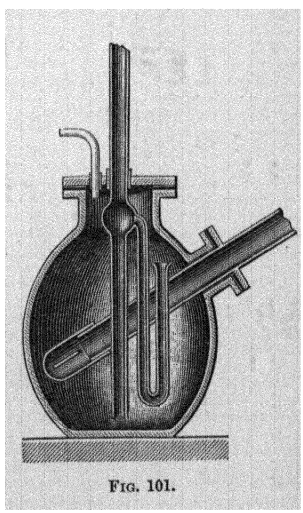
FIG. 101.

regulating both pulsometers so as to act together. Above all, valve *i* must be kept in order; for strong sulphuric acid it must be made of lead (regulus metal), and constructed very

carefully ; for chamber acid or hydrochloric acid it may be made of india-rubber.

This apparatus, once properly set, acts day and night without any supervision ; it is started or stopped in a moment by opening a tap.

Fig. 99 shows a pulsometer of 50 l. total and 40 l. available space. The rising-main must be 1⅜ in. wide ; in the case of a wider pipe, part of the acid would run back and air would rise. The apparatus can act thirty times per hour, and lift 25 to 30 cub. m. (say 875 to 1050 cub. ft.) per twenty-four hours. Fig. 100 shows an apparatus intended for greater speed. There is a rising-pipe, *a*, of 1 to 1⅜ in. width, provided with a valve, and a much wider feed-pipe, *c*, also provided with a valve. The latter must always be full ; the outflow thus takes place under the pressure of the liquid column *d e*, and therefore very quickly. Fig. 101 shows the form best adapted for stoneware vessels, which should stand a pressure of 4 atm.

Simon[1] describes a combination of two similar pulsometers which utilises the compressed air otherwise escaping during the filling of the vessel, the two being connected by a Y-pipe and automatic ball-valve.

The principle of the pulsometer has been improved by replacing the siphon by a float-valve. This type has been very carefully worked out by Paul Kestner, of Lille and London, and the present type of elevator is the outcome of long study of the problem.

Model "A" of the intermittent type, shown in Fig 102, is made of cast-iron for use with strong sulphuric acid or caustic soda ; for weaker sulphuric acid it is lined with lead, whilst for hydrochloric acid the lining is of ebonite.

Kestner also makes elevators in earthenware for raising nitric acid, the special feature being the method of connecting the float to the lever by means of a wire ; originally this was of platinum, but now wire of a special alloy is used.

The method of working, which is common to all types, makes use of the expansion of the air under diminishing pressure.[2]

[1] *Z. angew. Chem.*, 1890, p. 356.

[2] Extract from a lecture on the elevation of corrosive liquids given by B. Heastie, A.M.I.C.E., of Kestner's Evaporator and Engineering Co., London, at the Manchester School of Technology, December 1920.

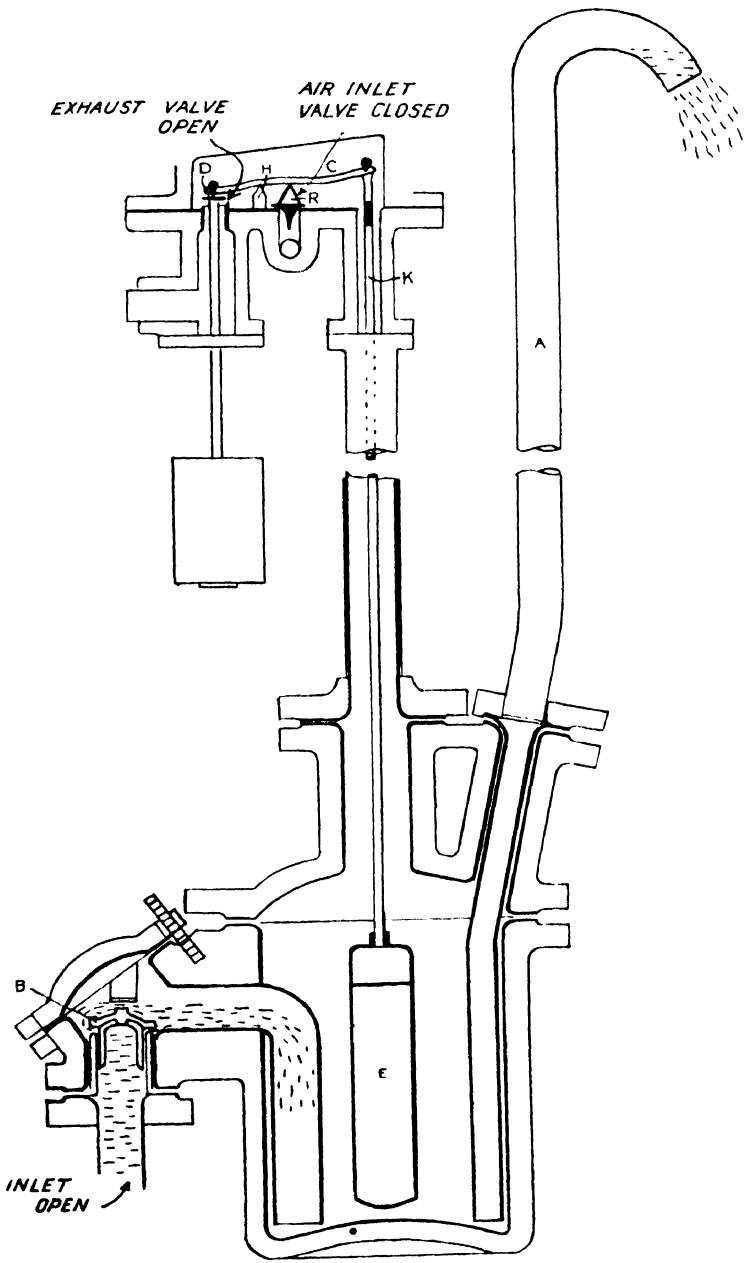
EXHAUST VALVE OPEN
AIR INLET VALVE CLOSED
D
H
C
R
K
A
B
E
INLET OPEN

FIG. 102.

The duty of the type illustrated is to raise 200 to 250 gallons of acid of 1·72 sp. gr. per hour to a total height of 80 ft. through a 1-in. diameter lead pipe, the available air-pressure being 70 lb. per sq. in. gauge (85 absolute).

The action of the elevator is as follows: The body fills with acid from the supply-tank and lifts the float E, which is connected by the rod K, to the lever in the elevator-head. The air-valve R now opens, admitting the compressed air. Immediately the air-pressure increases in the body, its effect is to close the acid inlet-valve B, cutting off the supply of acid and forcing the acid up the discharge-pipe A; this continues until the acid rises to a height of about 73 ft., when the whole of the acid originally contained in the body will have passed into the discharge-pipe, the air-pressure in the elevator having, in the meantime, increased from atmospheric to about 62 lb. gauge pressure.

The air-pressure now increases slightly, lifting the column of acid through the remaining 7 ft., and the acid commences discharging. As the discharge continues, the head of the acid in the discharge-pipe (and consequently the pressure in the elevator-body) decreases until the last drop of acid leaves, when the pressure drops to atmospheric.

By examining the valve mechanism, the movements whereby the air is admitted and exhausted are clearly seen.

The lever C works on a fulcrum H, and the rod K, which is coupled to the float, rises when the body is full. This at once releases the pressure from the air-valve R, and air is admitted into the head and passes down the stand-pipe to the body; at the same time the pressure of the air closes the air exhaust-valve D. The compressed air forces the acid from the body up the delivery-pipe to the receiving-tank. By the time the last drop of acid is discharged, the pressure in the elevator-body approaches atmospheric, and the pressure on both sides of the exhaust-valve now being equal, the weight of the float overcomes that of the balance weight, the float drops and the exhaust-valve opens; and as the back pressure is thus removed from the inlet-valve the acid rapidly refills the body and the cycle is repeated.

The acid-elevators already described are those which work intermittently, the same as the ordinary acid-egg, excepting

that they are automatic in operation. It is necessary, however, for delivering acid into sprays and for certain other purposes, that the acid should be delivered continuously. A continuous elevator was, therefore, designed by Kestner for this purpose. The lower portion consists of two bodies, one of which is slightly larger than the other, in order to contain a float operated by means of a simple valve.

These elevators are used for discharging acid through sprays, and are very simple in operation and have no working parts revolving in acid, the only parts subjected to the acid being the inlet- and outlet-valves.

Having considered the mechanical construction of the elevator, attention must now be drawn to its theoretical characteristics.

In practice, one usually has to design the elevator for a given duty, and also estimate the pressure and approximate quantity of air used, so that the correct size of air-compressor may be installed. The problem, therefore, may be subdivided into the following parts:—

(1) The pressure of air required to discharge the acid to a given height.

(2) The size of containing vessel, *i.e.* elevator-body.

(3) Size and capacity of discharge-pipe.

(4) Total time of emptying body.

(5) Total time of filling body from supply.

(6) The amount of free air required.

It will be appreciated that, in view of the number of inter-dependent factors involved, an exact solution will not be obtained, although one sufficiently close for designing purposes may be arrived at.

In the following investigation let—

(H) = Head in ft. through which the liquid is to be lifted.
(h) = The head loss due to friction.
(t_d) = The time required to fill discharge-pipe.
(t_f) = The time required to fill elevator-body from the feed-tank.
(t_x) = The time required to discharge contents.

It is impossible to determine the friction-head by direct calculation, and experience is the only guide. The friction of a viscous liquid in smooth pipes has been shown to bear a direct relationship to its absolute viscosity divided by its

density, *i.e.* the commercial viscosity as measured in a Saybolt or other flow-type viscosimeter. Therefore, the friction-head can only be determined if the temperature, viscosity, and velocity are known, but, as the velocity of discharge is dependent on the pressure obtaining in the elevator-body, which pressure is again dependent on the static and frictional head, it is sufficient in practice to assume a mean velocity of say 5 ft. per second, and obtain the friction loss from the curve and add this to the value of H.

A study of the flow of viscous liquids in pipes is extremely interesting, and the investigations of Pannell, Stanton, and Higgins, at the National Physical Laboratory, 1914 to 1916, together with the earlier work of Osborne Reynolds, show the great danger of applying the results obtained from experiments in hydraulic flow to the flow of viscous fluids.

Fig. 103 shows the friction-head loss through a 1 in. diameter pipe for water and sulphuric acid of sp. gr. 1·72. This curve was plotted from formulae deduced from the investigations referred to above, in which there is a definite relationship established between the absolute viscosity of the liquid and its friction-head loss.

Fig. 102 shows the third of the three stages in the operation of Kestner's elevator.

In the first stage, the body fills with acid from the feed-tank and the float commences to lift the air-valve, admitting compressed air into the body. Assuming that the air-pressure before entering is constant at 85 lb. absolute, it will begin to flow against a back-pressure of 14·7 lb. until the acid rises in the discharge-pipe, when the back-pressure will slowly increase until it becomes equal to the pressure due to the weight of acid in the discharge-pipe plus the (assumed) friction-head loss. The total contents of the elevator-body when displaced will rise to a height of 73 ft., the static pressure being 54·4 lb. per sq. in., whilst the friction loss has been assumed to be 14 per cent.

Thus the maximum pressure in the elevator-body will be 54·4 plus 14 per cent. = 62 lb. gauge, or 77 lb. absolute.

The time required to expel 0·4 cub. ft. of acid from the body into the discharge-pipes to the height of 73 ft. will be equal to that required for a weight of air measured at a

pressure of 77 lb. absolute, which would fill the elevator-body (0·54 cub. ft.), to flow through the orifice (in this case $\frac{1}{8}$ in.

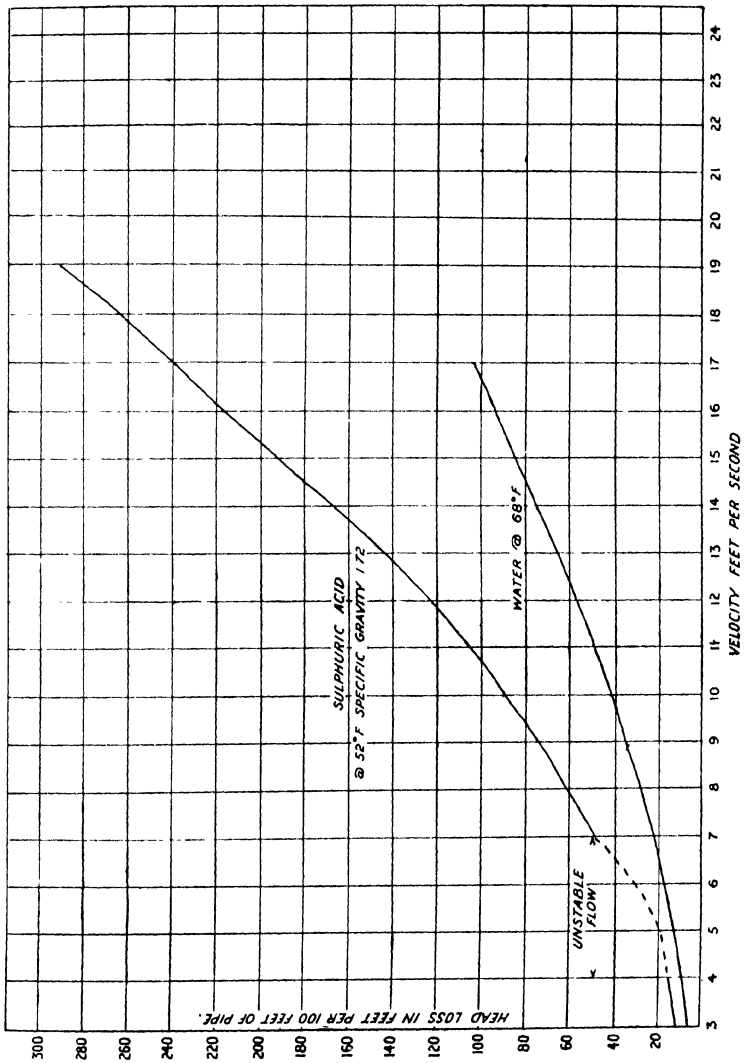

FIG. 103.

diameter) with an initial pressure of 85 lb. absolute, and a back-pressure varying from 15 to 77 lb. absolute.

From the curve, Fig. 104, showing lb. of air flowing per second, plotted against back-pressure, the average ordinate

between 15 and 77 lb. is obtained. Thus the average weight of air flowing per second is 0·016 lb. The weight of 0·54 cub. ft. of air at 60° F. and 77 lb. pressure is about 0·216 lb. Thus the time required to raise the acid 73 ft. is 13½ seconds. Further time is now occupied in lifting the acid a further 7 ft., viz. from 73 ft. to 80 ft., when it is then discharged. The inertia of the column of liquid due to its velocity will carry it through this distance in about 1½ seconds. The time yet required to complete the discharge must now be considered. This stage is carried out by the expansion of the air already in the body of the elevator, the air inlet having been closed by the falling of the float. At the beginning of this stage there is 0·54 cub. ft. of air at a pressure of 77 lb. per sq. in. absolute. At the end, when the last plug of acid is leaving, the air has expanded to fill the discharge-pipe and the body, which has a combined capacity of 0·978 cub. ft. Therefore, the pressure of the air at discharge is 27 lb. per sq. in. gauge and about 1·8 cub. ft. of free air are lost. The time occupied over this stage is short, as, although the initial velocity is about 5 ft. per second, the acceleration is considerable, being due to the fact that the head is decreasing much more rapidly than the pressure, and it is found in practice that about 6 seconds is required. One more stage completes the cycle of operation, viz. the filling of the elevator-body with acid. This is usually filled from a tank under about 4 ft. head, and, in the case under consideration, through a 1½ in. pipe.

A velocity of 2 ft. to 3 ft. per second may be assumed, the time of filling being thus 16 seconds.

Total time occupied for cycle of operations:—

Filling	16 seconds
Elevating to 73 ft.	13½ ,,
Lifting a further 7 ft.	1½ ,,
Discharging	6 ,,
	37 seconds

Thus the gallons lifted per hour would be 243.

In the above, no apparent account has been taken of the possible cooling and consequent contraction of the air after expansion, but in practice it is doubtful if this takes place to any great extent, as a certain amount of heat is generated by the friction through the orifice, which tends to raise the

temperature. The temperature of the air in the main is usually only a few degrees higher than that of the surrounding

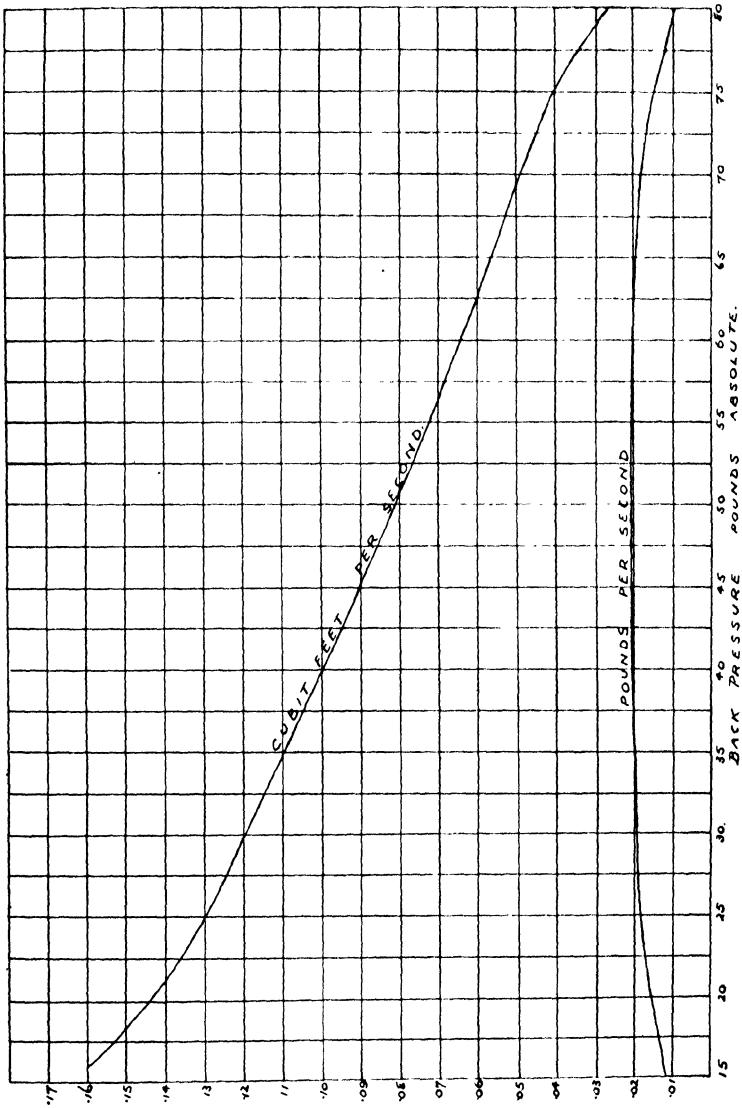

FIG. 104.

atmosphere, as the compressor and air-receiver are often at some distance from the elevator, and there is thus a considerable drop of temperature between these points.

Considerable economy can be effected by reheating the air with a steam heater when there is a supply of steam available. This method has been largely adopted by Kestner, who employs a special heater for this purpose.

By reference to a curve of adiabatic compression, it will be seen that, if air at atmospheric pressure and a temperature of 60° F. is heated to 278° F., the pressure increases to 50 lb. per sq. in. In conclusion, it will be of interest to determine the efficiency of the elevator. The total air used per cycle was 0·216 lb. This represents a volume of 2·83 cub. ft. free air at 60° F. The theoretical work required to compress this adiabatically to an absolute pressure of 85 lb. is about 12,700 ft. lb. The work done in lifting 2½ gals. of 1·72 sp. gr. acid against a total head, including 14 per cent. friction, of 91 ft. is 3100 ft. lb. The efficiency is, therefore, between 25 and 30 per cent., as the compression is neither truly adiabatic nor isothermal.

Of course, when working with such small quantities of air as are required in the process of elevating liquids in the manner described, such low efficiency is not of great importance. (W. W.)

The firm Paul Schütze & Co., at Oggersheim (Pfalz), manufactures automatic acid-eggs of a special construction which have stood the test of many years' practical experience. They are described in *Chem. Trade J.*, 1905, xxxvi. p. 90.

Plath has constructed an automatically acting acid-egg, supplied by the Deutsche Ton- und Steinzeugwerke at Charlottenburg (Ger. P. 159079). In *Z. angew. Chem.*, 1907, p. 1186 *et seq.*, he describes several modifications of it.

Some improvements in apparatus for raising liquids by air-pressure are described in the B. P. 10051, of 1907, by Scherb.

C. Simon, of Stolberg, has constructed a pneumatic acid-pump, provided with an automatically acting piston-governor, which is stated to be superior to the regulation by floats in various respects. *Cf.* also Plath on mechanical means for raising acids, *Z. angew. Chem.*, 1902, p. 1311.

The Badische Anilin- und Sodafabrik (Ger. P. appl. B60169) employ for their acid-eggs an automatically moving governor-tap, which is set into motion by a mercurial differential pressure-gauge.

A review of progress in the construction of automatic apparatus for raising liquids by compressed air is given by Deimler in *Chem. Ind.*, 1911, pp. 39-46.

Pumps.

There are two types of pumps made by Kestner for pumping acid :—One is the centrifugal type, Fig. 105, and the other the plunger type, Fig. 106. Both these pumps embody the same

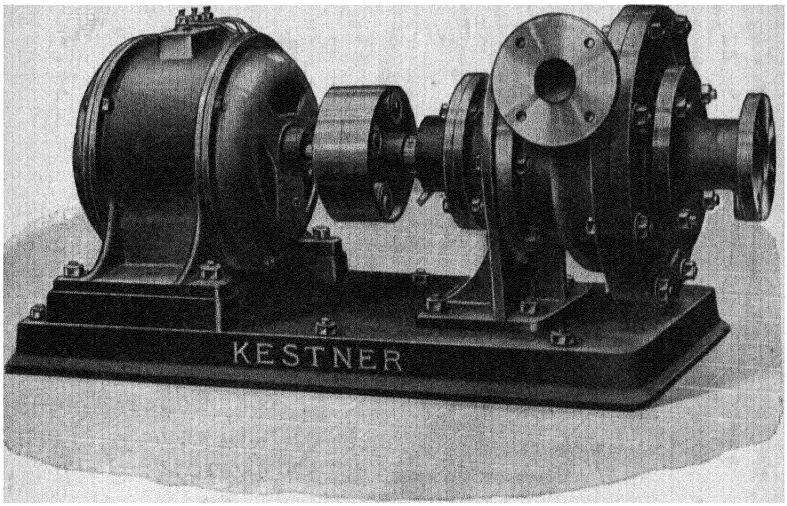

FIG. 105.

important feature, whereby they differ from all other types of pumps for dealing with acids.

Every one will admit that the difficulty in designing a suitable acid-pump is due to the trouble with the glands. In the case of the centrifugal pump, the gland is on the pump-shaft, and in the case of the plunger-pump, it is on the piston-rod, or around the plunger. Kestner eliminates all glands and substitutes instead, in the case of the centrifugal pump, an arrangement of a sleeve, in which the shaft revolves; and in the case of the plunger-pump, a sleeve through which the plunger passes. There is, however, a small but definite clearance allowed between the sleeve and the shaft in the one case, and the sleeve and the plunger in the other. Moreover, Kestner utilises the liquor itself which is being pumped as the lubricant

and arranges a definite leakage, which is very small, being about 1 litre in two or three weeks. The pump-bodies themselves can be made in regulus, cast-iron, or silicon-iron, according to the nature of the liquor to be dealt with, but in every case this arrangement of the sleeve is utilised, and, being constructed in acid-resisting metal, it is absolutely reliable in operation. Kestner mentions a case where one of these pumps was left standing for some weeks under a considerable pressure from an overhead tank, and no sign of leakage was observed.

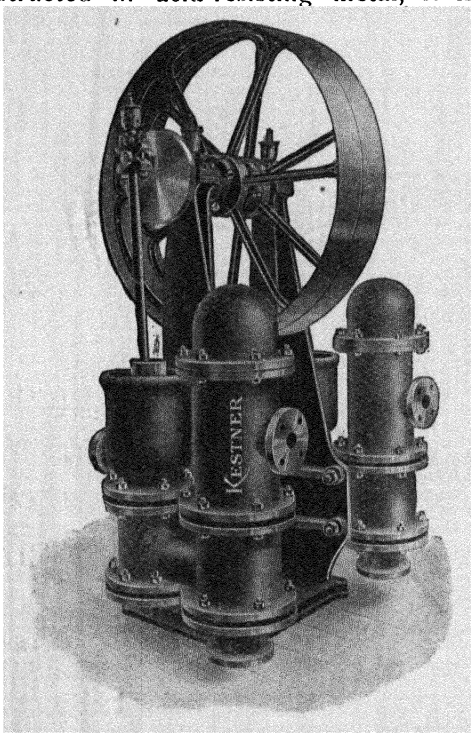

Fig. 106.

The Ferraris Acid-pump (B. P. 4482 of 1914, and Fr. P. 457936) appears to be displacing the acid-egg, especially on the Continent. The piston runs entirely in oil (Fig. 107), and at very low speed, namely from 9 to 11½ revs. per minute. Its efficiency is said to be 96 per cent. and the repairs and supervision very slight. These pumps are made in capacities of from 220 gals. to 1980 gals. per hour, and require from ½ to 2 h.p. to drive. Their action is very simple. When the piston *a* rises, the oil is drawn into the piston-bucket, and an equal volume of acid enters the column. Upon the piston returning, the aspiration-valve *b* closes, and the delivery-valve *d* opens, the acid thus being forced forward. There is no disturbance to its working should the acid supply fail at any time.

Some 700 pumps have already been supplied by Benker & Millberg, of Asnières, near Paris.

An acid-pump [1] of new design is manufactured by the Duriron Co. of Ohio. The main features of this pump are :—

(1) Packing under slight vacuum while the pump is in operation. (2) A helical impeller. (3) Accessibility of

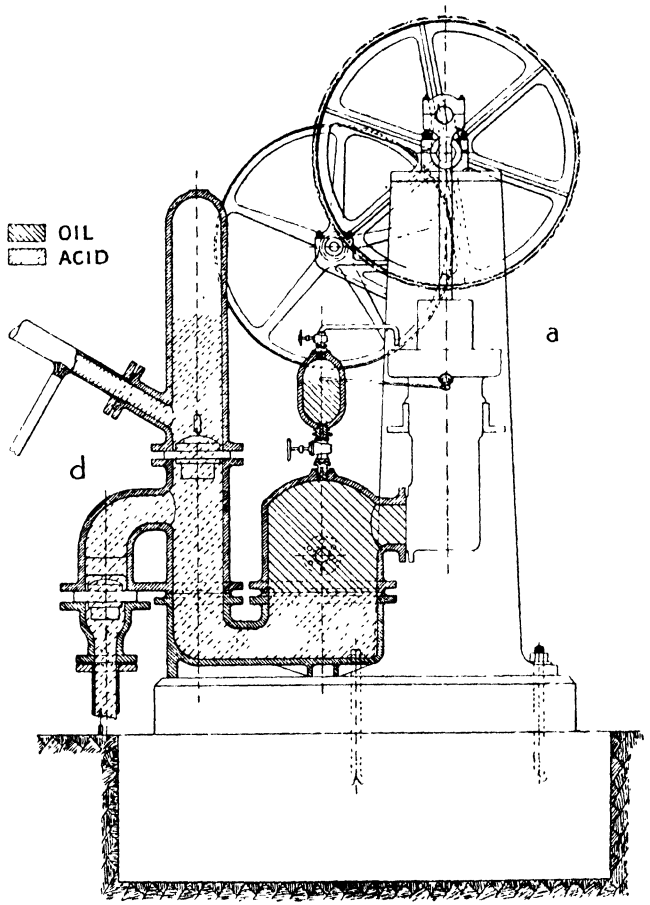

FIG. 107.

revolving parts without disturbing either suction- or discharge-line. (4) Rotatability of both volute- and suction-elbow to any position desired, in order to fit existing pipe-lines.

In this pump it is claimed that the packing cannot be

[1] Described by A. M. Fairlie, *Chem. and Met. Eng.*, 25 (1922), 967.

touched by the acid while the pump operates, inasmuch as the stuffing-box is under a slight vacuum. However, if the pump should be stopped without first closing a valve at the bottom of the discharge-line, it is likely that here, as with all other horizontal shaft-pumps, some acid might enter the stuffing-box and cause slight leakage.

The speed of the pump can be regulated to deliver any quantity up to the maximum capacity. After removing the cover-plate from the side of the pump opposite the stuffing-box, the runner and shaft can be removed without disconnecting either the inlet- or the outlet-pipe. The shaft is of machine steel, and is covered by a "duriron" shroud projecting through the stuffing-box. A web cast between the top of the volute and the discharge-flange, is designed to permit the escape of trapped air and prevent air-locking.

The pump is fitted for either direct-connected motor- or for belt-drive.

Guthrie & Co., of Accrington, make several types of pumps suitable for pumping corrosive liquids. We will only describe their glandless pump which has recently been placed on the market. It is reinforced with their ceratherm-porcelain material.

Ceratherm is a new acid-ware, which was prepared during the war for rapid condensation of large quantities of acid-gas in the manufacture of explosives. It has useful properties which make it suitable for this work, in that small articles can be heated to a red heat and plunged into cold water without cracking, and it conducts heat much more quickly than ordinary stoneware, thus enabling an equable temperature to be maintained throughout any apparatus into which it is made.

A blow on a piece of ceratherm does not produce the same shattering effect as on a piece of glass or a piece of highly vitreous stoneware.

The type of ceratherm used for the manufacture of pumps, however, is not the same as that used for the manufacture of Hart's nitric-acid condensing plant, for instance, but a type was prepared with considerably increased tensile strength. Sufficient of the heat-resisting capacity of the original form of ceratherm has been retained to enable the pump to be worked

alternately on hot or cold liquids without any liability to fracture.

Other advantages are, that the new type of ceratherm can be manufactured more accurately and lends itself to the preparation of very thick, strong apparatus. The ceratherm is, of course, entirely unaffected by practically any chemical, and the liquid being pumped does not come in contact with any other material but the porcelain. The new pump has no valve, gland packing or stuffing-box, and requires very little attention.

In the event of the mechanism driving the pump becoming inoperative from any cause, there is no danger whatever, or loss of liquid. Instead of a stuffing-box there is a large tray which may or may not be connected to another tray slightly larger than itself. These trays contain a few gallons of liquid. The shaft is covered during the whole of its length as it passes through this liquid to reach the impeller. Where the shaft passes through what is in the ordinary case the stuffing-box, there is nothing but a close fit. A by-pass from the delivery-pipe of the pump delivers a small stream of liquid into the tray which passes through the pump, and in that way what is in the ordinary pump the gland is maintained absolutely free from air and kept sealed by the liquid which the pump itself is circulating.

In the neighbourhood of 40 ft. head, efficiencies of 60 per cent. have been attained. In the neighbourhood of 120 ft. head, efficiencies of 40 per cent. have been obtained even with the diminished quantities required by the acid-makers. If large quantities are required, very high efficiencies could probably be attained at high heads, say in the neighbourhood of 70 per cent.

The following table shows the capacities, etc., of these pumps:

	Revolutions.	Head Feet.	Quantity. Galls. per min	H.P.	Efficiency.
N1	1750	116	160	13¼	43 per cent.
N2	1400	87	110	6	48·3 ,,
N3	1750	128	120	12¼	38 ,,
N4	1000	35	160	2¾	62 ,,
Q	1665	35	150	2¼	71 ,,
Q1	1450	35	100	1¾	60 ,,

The centrifugal pumps supplied by Simon-Carves are more

suitable for strong sulphuric acid. They are made wholly of cast-iron with the exception of the shaft, which is of steel protected by an easily removable cast-iron sleeve. They are arranged either for belt drive or directly coupled to an electric motor. Their capacity varies from 50 to 130 gals. per minute according to the height of delivery.

Moritz (Fr. P. 441304) places the pumps, made of an acid-resisting material, within the acid contained in the reservoir, by which means many troubles otherwise occurring in the pumping of the acid are stated to be avoided.

Nagelschmidt (Ger. P. 279074) avoids the jerks and splashes in pumping by applying an intermediate pipe between the lower acid-reservoir and the "emulsioner," and a pulsometer between the emulsioner and the top reservoir.

The "Mammoth-pump" of the engineering works, A. Borsig, at Tegel, near Berlin, is specially recommended for pumping acids, as it has no valves or other moving parts.[1]

Haughton's Patent Metallic Packing Co., Ltd., 30 St. Mary-at-Hill, London, sells centrifugal pumps made of a material completely resisting the attack of acids.

The Oliver-Sherwood Co. has designed the "Olivite" centrifugal pump, which embodies the features desirable in a pump suitable for corrosive liquids (Fig. 107*a*). Olivite is a substance having a rubber base, but possessing a combination of qualities seldom found in other material. It has all the chemical resistant qualities of hard rubber, but none of its inherent physical defects. It is not brittle, has a high tensile strength, and is ideally adapted for handling corrosive solutions even under high temperatures.

The stuffing-box construction permits free shaft movement without undue distortion of the packing used in the gland, and also allows the packing to follow the shaft through any of its eccentricities without excessive tightening upon the gland nuts.[2]

[1] Described in *Chem. Zeit.*, 1914, p. 274.

[2] Further information regarding the pumping of corrosive liquids in chemical works is given in the *Proc. Chem. Eng. Group* (Soc. Chem. Ind.), 1 (1919), by J. A Reavell, pp. 38–42; R. Stewart, pp. 42–44; J. H. West, pp. 51–73; W. Hayhurst, pp. 73–76; and S. J. Tungay, pp. 47–50; and more recently by Clark S. Robinson, *Ind. and Eng. Chem.*, 15 (1923), pp. 33–38.

J. Oliphant [1] describes the *air-lifts* on the principle of those used for artesian wells, their use having extended for elevation of corrosive acids. The principle of the air-lift is to lighten the column of liquid in the eduction-pipe with air, so that the weight per square inch of the eduction-column mixed with air at the jet is less than the submergence head. For a low percentage of submergence, more air must be used than with a high percentage for the same lift, in order to keep the weight

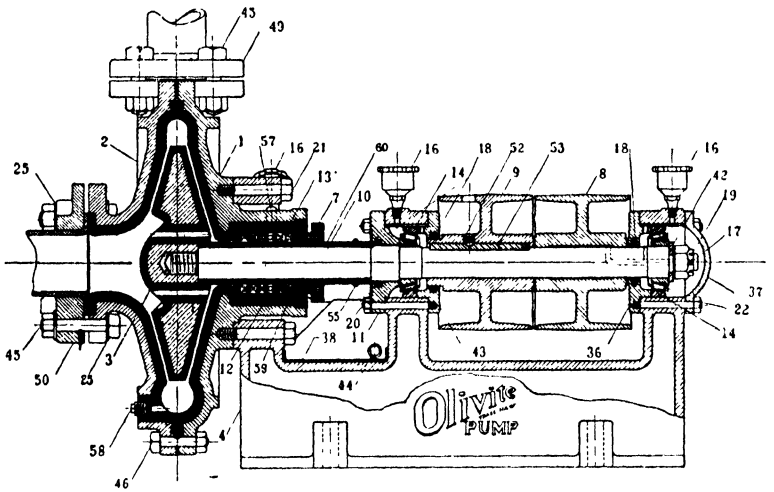

FIG. 107*a*.

LIST OF PARTS.

1. Casing.
2. Cover.
3. Impeller.
4. Base.
7. Gland.
8. Loose Pulley.
9. Tight Pulley.
10. Shaft.
11. Flange.
12. Lantern Ring.
13. Packing.
14. Timken Bearing.
16. Grease Cup.
17. Cotter Pin.
18. Felt Washer.
19. Castle Nut.
20. Stud.
21. Capscrew.
22. Stud.
25. Washer.
36. Thrust Yoke.
37. Shaft Cap.
38. Olivite Drip Can.
42. Washer.
43. Thrust Yoke.
44. Olivite Nipple.
45. Bolt—Flange.
46. Bolt—Casing.
49. Companion Flange.
50. Companion Flange.
52. Headless Set Screw.
53. Key.
54. Gland Bolts.
55. Drip Ring.
57. Nipple with Sleeve.
58. Plug.
59. Stuffing-box.
60. Non-corrosive Sleeve.

of the eduction-column below this. However, with low submergence a lower pressure is required, so that the power is theoretically equal. For low submergence, more careful design is necessary, but with acid of high temperature or gravity the difficulties are less than with water.

The air should be applied by a large number of fine jets

[1] *Chem. and Met. Eng.*, **22**, 408-410.

into a thin sheet of fluid and, by careful installation, the efficiency should reach 30 to 35 per cent. Whilst this can be exceeded by mechanical pumps under test conditions, it is found, under actual practice, that the air lift is more efficient and maintains its efficiency at a higher point, after a short period of operation. This is on account of the detrimental effect of the acid on mechanically operated pumps of either the centrifugal or the plunger type. At the same time the cost of repairs and attendance is eliminated in the case of the air lift.

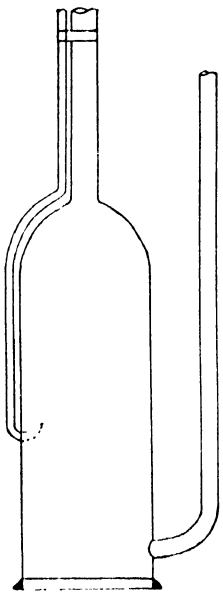

Fig. 108.

Where it is impossible to lift in one stage owing to the difficulty of sinking the lifter, it is necessary to use two or more lifts, and therefore separators are placed at each height and the fumes and air carried to the chambers or towers or any other point desired. In the original paper a graph is given showing the capacities for the various sizes of air and acid mains with the necessary pressure.

For circulation of acid from one chamber to another, a very simple form is illustrated below, and is constructed and fitted up in the course of a few hours (Fig. 108).

The construction of *tanks or reservoirs* for sulphuric acid is the next consideration. *Open* reservoirs for sulphuric acid are invariably made of lead, usually consisting of a strong wooden frame to which the lead sides are fixed by means of straps, the upper edge being turned over the top, just as in the construction of chambers, or else a box made entirely of wood with lead lining (see Fig. 97, p. 172). In each case the thickness of the lead need not exceed 6 or 7 lb. per superficial foot, if the wood frame is so constructed as to take all the side thrust; but it is preferable to use thicker lead, say 9 or 10 lb., on account of wear and tear. Where it is intended for hot acid to run into the tank and cool there, the tanks are preferably made circular in shape, of much thicker lead (say 10 lb. or

more), and strengthened on the outside with strong iron hoops, which may be connected by strong cross-stays in the case of very large tanks. Considering the increase of pressure from the top downwards, the binding-hoops should be placed nearer together in the lower part of the tank.

Even *brickwork* may serve for acid-tanks (sulphuric, hydrochloric, nitric acid), if the bricks, tiles, stones, etc., are acid-proof. Volvic lava is the best material (*cf.* later). The mortar in this case should be a paste made of asbestos powder and silicate of soda solution, with or without some other solid admixture, as barytes, etc. This mortar should not at first be brought into contact with water, which would dissolve out the sodium silicate, but at once with acid, which causes silicic acid to separate in the solid state and to render the joints perfectly tight.

For *closed tanks* for sulphuric acid the best material is *iron*, either cast or wrought, as may be most suitable for constructive purposes; and this material is also adapted even for *pipes*, etc., in cases where no air can enter, as the moisture of the air might dilute the acid, which ought not to be below 120° Tw.

Working the Gay-Lussac Tower.

After the above explanations little need be said as to the working of the absorbing-tower. The following points have to be observed in this respect.

The *gas* entering the tower must show a distinctly red colour in the "sight." On the other hand, the exit-"sight" should show a perfectly colourless gas. The gas escaping from the top of the tower, or of the chimney connected with it, ought not to produce any considerable amount of red vapours when it meets the outer air (see below). Furthermore, the chamber-gas before entering the tower should be as *dry* and as *cool* as possible, lest the absorbing-acid be diluted or heated. For this purpose, the last chamber receives very little, sometimes even no steam, so that its acid remains at about 106° Tw.; moreover, the gas is often conducted through a long pipe or a tunnel, or into a shallow box with several baffles, where it has to move backwards and forwards. In these cooling-apparatus, water may be applied outwardly to assist the cooling, especially in summer-time. Sometimes the bottom of the box is covered

with strong vitriol, in order to dry the gas; this, however, to a certain extent, only anticipates the tower. Hartmann and Benker[1] employ a tubular cooler for the same purpose. The *sulphuric acid* serving for absorption must be at least 144° Tw., but this is only a minimum, which ought to be exceeded if possible. Acid of 148° absorbs much better, that of 150° or 152° Tw. better still. Wherever possible, acid of 152° Tw. should be employed for the absorbing-process. This acid can be got without any difficulty from the Glover tower.

Coolers.

Above everything, care must be taken that the acid used for absorbing is as *cool* as possible. Hot acid absorbs very badly, a large amount of nitre is lost, and at the same time a weak nitrous vitriol is produced. At the French works they believe that 25° is the best working temperature. It is therefore necessary either to provide a very large tank for cooling the acid, concentrated in pans or in the Glover tower, before it is used in the Gay-Lussac tower, or (as the cooling by mere exposure to the air is a very slow process, especially in summer, and in large works enormous tanks would be required for it) special cooling-apparatus is employed. Many works use double spouts—an outer one filled with water, and an inner one, in which the hot acid travels. In this case, it is rarely possible to apply the rational principle of running the cooling-water in a current opposite to that of the acid to be cooled, because, on account of the length of the spouts, there is no fall for this. These double spouts also have a disagreeable tendency to swell out at the bottom whenever a little more pressure takes place, because the lead when hot diminishes in strength.

A very efficient cooling-apparatus is constructed as follows:—

A shallow pan about 20 ft. long by 8 ft. wide by 9 in. deep lined with 7-lb. lead is placed upon an elevated position commanding the storage tanks. It is preferably made of 3-in. planks well bolted together. Into this is placed a long trough 10 in. wide by 6 in. deep, made of 20-lb. lead, the trough being carried backwards and forwards and occupying the whole of the

[1] *Z. angew. Chem.*, 1906, p. 136.

pan. The trough is supported at intervals about 1 in. off the bottom of the pan, in order to allow for better cooling. Water circulates around the troughs and underneath, thus giving a very efficient cooler. The advantage of the wide troughs is in

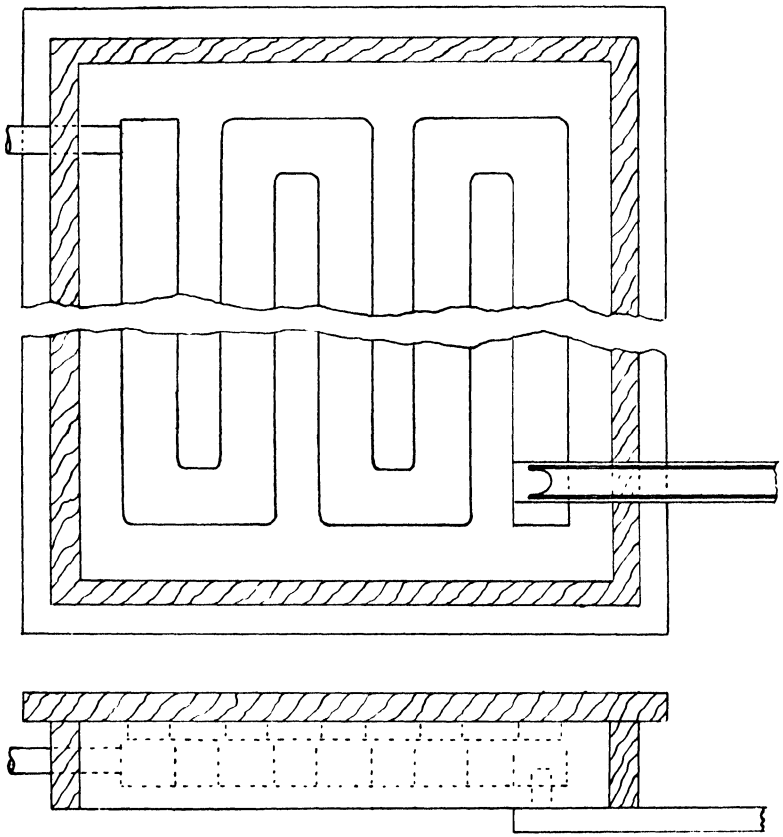

FIG. 109.

the ease with which any deposit can be removed by shovel without stopping the flow of acid.

Fig. 109 illustrates the arrangement and needs no further description.

The use of coolers containing water-coils has little to recommend it.

Crowder[1] describes a cooling-arrangement, and gives details

[1] *J. Soc. Chem. Ind.*, 1891, p. 300.

concerning its function. The acid travels altogether about 1000 ft., and its temperature is brought down from 139° or 149° to 28° or 39°. Further on (p. 304) he contends that such cooling is unnecessary (except, perhaps, in order to save the lead from quick corrosion), on the strength of laboratory experiments in which acid of sp. gr. 1·75 did not absorb the nitrous vapours from chamber-gases much less at 100° than at the ordinary temperature. As, however, he never went beyond 0·47 or at most 0·69 per cent. N_2O_3 in the acid, his statements are not to the point. It has been proved by experiments made on the nitrous-acid tension of sulphuric acid that this increases rapidly with the percentage of N_2O_3, and in all cases with the rise of the temperature. In case of such low percentages of N_2O_3 as those employed by Crowder, the tension of N_2O_3 is not very great even at higher temperatures; but in actual work higher percentages of nitre must be aimed at, in which case any higher temperature of the acid would act injuriously. This has been fully confirmed by observations communicated by Hasenclever.[1] A high temperature not merely prevents the absorption of N_2O_3, but even expels it from stronger nitrous vitriol.

Very efficient cooling might be produced by the action of a current of air, either by forcing this through the hot acid, or else by running the hot acid down a tower in which air rises up by the action of a fan or by chimney draught; but where very large quantities have to be treated, the supply of cooling-air might be too expensive.

In ordinary circumstances the absorption in the Gay-Lussac tower requires *at least* one-half of all the acid produced. This is obtained from the Glover tower without any other cost than that of pumping; in the case of other denitrating apparatus the cost of concentration has to be added to this. Frequently the necessary quantity of absorbing-acid is stated at a lower figure—for instance, as one-third of the whole production; but this in most cases is certainly insufficient, and no doubt a large loss of nitre would result from it. On the other hand, manufacturers working with Glover towers, who, apart from the trifling expense of pumping, have no concentrating-expenses at all, send all their acid once a day through the Gay-Lussac

[1] *Chem. Ind.*, 1893, p. 337.

tower. Bode[1] calculates that with a loss of four parts of nitre or 1·75 of N_2O_3 to 100 parts of acid of 168° Tw., the absorption requires at least 56 per cent. of *all* the acid of 144° manufactured, if very strong nitrous vitriol (with 1·75 per cent. of N_2O_3) is to be obtained. Such strong nitrous vitriol, however, is not obtained in ordinary working; and therefore considerably more than 56 per cent. of all the acid manufactured must be run through the Gay-Lussac tower in order not to lose any nitre. In fact, some manufacturers send much more than their daily make through the Gay-Lussac towers, but at some of the best-conducted works they manage with about four-fifths or five-sixths of the daily make. Of course, everything depends upon the style of working the chambers. With the ordinary style, where there is about 12 cub. ft. of chamber-space to each pound of sulphur burnt in twenty-four hours, the figures quoted above are quite sufficient; but the forced or high-pressure style of work, where there is about half that chamber-space (p. 45 *et seq.*, and below), cannot be kept up except by a very large floating capital of nitre, and in this case twice or more the daily production of acid has to pass through the Gay-Lussac tower. (See Thede, p. 48, who circulates ten times the production of acid.)

The specific gravity of the *nitrous vitriol* issuing at the foot of the Gay-Lussac tower does not differ very much from that of the acid fed in at the top. In the usual case, where there is ample chamber-space and the sulphuric acid is almost entirely condensed in the last chamber, the mixture still necessarily present in the exit-gases is, of course, absorbed by the stronger acid in the Gay-Lussac tower, and the nitrous vitriol running out at the foot is then 1° or even 3° Tw. weaker than the feeding-acid; but in the "forced style" of working (p. 45) there is a considerable quantity of acid contained in the exit-gases in the form of mist, which is retained in the Gay-Lussac tower, and, added to the nitrososulphuric acid absorbed, may make the nitrous vitriol even a little stronger than the feeding-acid.

When properly treated, nitrous vitriol ought not to be highly coloured, and should have only a slight smell of nitrous acid; but on being diluted with water, especially hot water, it ought

[1] *On the Glover Tower*, p. 49.

to effervesce strongly and give off red vapours. At some works this rough test is considered sufficient for judging the quality of the nitrous vitriol; but at all the better-managed works it is tested in the laboratory, which can be accomplished in a very short time by the permanganate method (*cf.* p. 300 of Vol. I). Occasionally this test should be supplemented by testing in the nitrometer, in order to make sure whether any nitric acid is present or not. By these testings it can be seen from day to day whether the percentage of nitre increases or decreases. In the former case, if the other tests of the chamber-process agree with it, this is an indication that some of the nitre must be taken off; in the latter case this test will, better than any other, show, before any damage has been done, that more nitre is required. In any case, nitrous vitriol should not contain less than 1 per cent. of N_2O_3; above $2\frac{1}{2}$ per cent. it is too strong, and there is danger of nitrous gas escaping without being absorbed; this can be controlled, however, by the colour of the exit-"sight." In this case, more strong acid must be charged at the top, and if there is an excess of nitre-gas in the chambers a little less nitre must be used.

The Gay-Lussac acid, or nitrous vitriol, is essentially a solution of nitrososulphuric acid ("chamber-crystals") in sulphuric acid. Formerly it was believed that it regularly contained some nitrogen peroxide or nitric acid (Winkler, Kolb, Hurter, Davis, etc.). This belief was, however, only due to the imperfection of the analytical methods employed, as was shown for Winkler's and Kolb's results by Lunge,[1] who proved that the nitric acid was produced during the analysis. The contrary, that *ordinary* nitrous vitriol contains no appreciable quantity of nitric acid, was first proved by Lunge, and has been confirmed by several subsequent investigators. This is even the case when so much nitre has been introduced intentionally, as in Lunge and Naef's experiments, or by inadvertence, that the last chamber contains some nitrogen peroxide.[2] It has been shown before (pp. 265 of Vol. I and 152 this Vol.) that this is no doubt due to a reduction of the nitric acid, originally formed from the nitrogen peroxide, by the coke packing of the Gay-Lussac towers. In the case of columns filled with

[1] *Chem. News*, 36, 147.
[2] *Chem. Ind.*, 1884, p. 10.

a non-reducing packing, probably nitrous vitriol containing nitric acid would be much more frequently met with; but with coke-towers, and with the ordinary style of working formerly employed in all works, it is one of the signs of the regularity of the process if *no* nitric acid occurs in the nitrous vitriol. Probably it is different when working with the "high-pressure" style (p. 45), where the chambers are made to turn out nearly twice as much as before, by supplying them with a comparatively enormous quantity of nitre (without, however, losing more of it in the long run, owing to correspondingly large Gay-Lussac towers). In this case it follows most distinctly, from Lunge and Naef's observations (next chapter), that there must be a *large* quantity of nitrogen peroxide in the last chamber, too large to be completely reduced by the coke to N_2O_3, so that the nitrous vitriol will be found to contain some nitric acid.

A misapprehension existed for many years, in all publications on the subject, and in the ideas of nearly all those practically concerned in the manufacture of sulphuric acid who gave any attention to the chemistry of the subject. This was that nitrogen peroxide, N_2O_4, forms only a "loose" combination with sulphuric acid of the concentration employed for working the Gay-Lussac tower, and that, therefore, very little N_2O_4 is absorbed in that tower, unless it can be reduced there by SO_2 to N_2O_3. This erroneous assumption, coupled with another error, viz., that the "nitre" in the chamber exit-gases consists essentially of N_2O_4, and the *true* observation that the "nitrous vitriol" generated in the Gay-Lussac tower does not contain anything but N_2O_3, led to the procedure of Brivet, Lasne, and Benker (Ger. P. 17154), which introduces a certain quantity of burner-gas into the exit-gases, on their way between the last chamber and the Gay-Lussac tower. This is done by means of a steam-jet. The excess of moisture thus imparted to the burner-gas is removed by a small coke-tower fed with Glover-tower acid, and the gas is then mixed with the chamber-gases before entering the Gay-Lussac tower. It was supposed that the nitrogen peroxide would thus be reduced:

$$N_2O_4 + SO_2 + H_2SO_4 = 2SO_2(OH)(ONO).$$

No doubt this would be the case if an appreciable quantity

of "free" N_2O_4 did exist in normal exit-gases; but this is not so, at least with the ordinary, not "forced" (high-pressure) work. Lunge has, moreover, conclusively proved[1] that there is no foundation for the assumptions underlying the patent mentioned above, more especially the idea that N_2O_4 did not easily and completely dissolve in sulphuric acid of 142° Tw. In fact, the first favourable reports upon the practical success of that patent process have not been confirmed by subsequent observations, and it must be held that, for properly-managed chambers, the process offers no advantage.

Benker has several times reverted to proposals, founded upon the alleged difficulty of absorbing N_2O_4 in the Gay-Lussac tower, to introduce SO_2 at some place where it is to reduce N_2O_4 to N_2O_3. He has, however, found that this cannot be done in the Gay-Lussac tower itself, and he therefore injects SO_2 into the last chamber or a special chamber placed between this and the Gay-Lussac tower (Ger. P. 88368). The mixture of gases in this case should be very thorough, and he therefore prefers to employ the SO_2, not as burner-gas, but in the form of a large quantity of gas from the first chamber, where much SO_2 is still present (Ger. P. 91260). This last idea is evidently much the same as the various proposals formerly made for mixing the chamber-gases from different parts of the system (*supra*, p. 56 *et seq.*).

U. Wedge (U.S. P. 1106999) also states that a certain percentage of sulphur dioxide in the gases leaving the last chamber generally improves the recovery of the nitrogen compounds. At 18°, 0·01 per cent. SO_2 by volume is sufficient; at 38°, 0·15 per cent. SO_2 by volume is required. He tests the gases before entering and after leaving the last chamber for their content of SO_2, and the proportion of this gas to the other ingredients is thus regulated.

The success of the working of the Gay-Lussac tower depends also upon the proper *regulation of the draught.* If the draught is insufficient, the chamber-process will, from the outset, be injured by the continual leakage of gas and by all the other drawbacks already enumerated, and specially by the behaviour of the pyrites in burning. With insufficient draught the Gay-Lussac tower itself will not work properly, for unless

[1] *Berl. Ber.*, 1882, p. 488.

a sufficient excess of oxygen is present in the last chamber before the gas leaves it, unoxidised nitric oxide will remain, which passes through the tower unabsorbed and only forms red vapours when it issues into the outer air. At the same time there will be an excessive amount of sulphur dioxide present, and this acts still more harmfully, since it decomposes the nitrosulphuric acid still present in the vitriol and carries away its nitre as nitric oxide. If the waste gas, as previously insisted upon, contains 5 or 6 per cent. of free oxygen, this cannot happen to an appreciable extent.

If, on the other hand, the draught is too strong, and therefore the kiln-gas is too poor, the sulphur dioxide will not have time to condense within the chambers as sulphuric acid. It will partly get into the tower, and there cause the decomposition mentioned above and a loss of nitrous compounds.

In both cases, therefore, the same result will follow as when the last chamber does not contain an excess of nitre-gas; and if the economy of nitre is cut too fine all the more will be wasted, the sulphurous acid driving off the nitrogen of the tower-acid into the air in the form of nitric oxide.

Such a *faulty working* of the tower will reveal itself by the escape of a large quantity of red vapours out of the chimney, by the tests of the tower-acid, and even by its appearance, since the acid, which otherwise is nearly or quite colourless, turns a dark purple colour, and is filled with countless small bubbles of nitric oxide, at the same time getting heated by the formation of sulphuric acid.[1] The worst conditions are, therefore, when the tower alternately receives gases containing sulphur dioxide and gases containing nitre. In that case, nitrous vitriol is alternately produced and again decomposed. When, however, sulphur dioxide constantly passes into the tower, there is no absorption of nitre-gas at all, and the tower in this case does not act as an absorbing-apparatus, but simply as a continuation of the chamber-space.[2] This proves, as Bode justly remarks, that one improvement necessarily led to another, viz., the recovery of the nitrous acid and a better condensation of the sulphur dioxide, or a better yield on the sulphur burnt.

[1] Bode, in a note to the translation of H. A. Smith's pamphlet, p. 122.
[2] Bode, *ibid.*, p. 124.

The loss of nitre caused by this imperfect action has been often underestimated, especially formerly when the methods for testing the exits were defective; indeed the very reasons which impede the full action of the Gay-Lussac tower will cause similar losses during the bubbling of the exit-gases for the purpose of testing through the absorbing-liquids on the small scale. It is quite certain that the loss of nitre in the exit-gases indicated by Jurisch and others, is far below the truth, and that this by itself vitiates most of the reasoning concerning the "chemical loss" in the Glover tower. Benker[1] has found that the Gay-Lussac sometimes allows two-thirds of the nitrous gases to escape, and Sorel[2] agrees with him, on the strength of calculations founded upon the vapour-tension of N_2O_3 in nitrous vitriol. He found this *unavoidable* loss to cover very nearly the whole loss of nitre in his chamber-system, viz., 2·66 per cent. out of 2·8 per cent. $NaNO_3$ for 100 S, leaving practically no "chemical loss," since only a little nitre escapes with the sulphuric acid withdrawn for use or sale.

Petersen claims to avoid disturbances in the "intense working" of the chambers by his "regulator" which is described and illustrated *supra*, p. 46.

According to the *Alkali Inspectors' Report* for 1909 several factories had obtained satisfactory results by the introduction of Petersen's "regulator" in respect of cooling the gases and completely utilising the SO_2. Petersen later (Ger. P. 225197), in order to economise Glover-tower space, recommends denitrating the nitrous vitriol, formed in the regulator and in the principal Gay-Lussac tower, in one and the same Glover tower. In this case the regulator is fed with chamber-acid. His Ger. P. 226793 states that the sulphuric acid in the Gay-Lussac towers is most fully utilised by converting the ferrous sulphate contained in the acid into ferric sulphate, before employing it for retaining the last portions of the nitrogen oxides.

The *exit-gases issuing from the Gay-Lussac towers*, even when these are of very large dimensions, are never free from either sulphur or nitrogen acids, and must be regularly tested to comply with the demands made by law, as will be described subsequently.

[1] Quoted by Sorel in his *Traité*, p. 313. [2] *Ibid.*, pp. 313 and 393.

It is unreasonable to expect the Gay-Lussac tower to retain absolutely the last traces of acids, especially the nitrous fumes, for the following reasons:—(1) A solution of N_2O_3 or of HSO_5N in sulphuric acid of 140° Tw. possesses a certain vapour-tension which causes some N_2O_3 to be volatilised in a current of air (*cf.* p. 259, Vol. I). (2) The contact of the gases with the acid can never be made absolutely perfect. (3) The time during which this contact takes place is very short. Sorel [1] calculates that for the best and largest apparatus, two minutes as a maximum is necessary.

It is a well-known fact that, at the very best managed acid-works, the gas issuing from the Gay-Lussac tower has a slight ruddy or orange colour, most of which is probably caused by NO, which finds too little oxygen within the tower, but turns into NO_2 in contact with air. Most acid-makers regard it, from experience, as a bad sign for the working of the chambers, if the orange vapours entirely cease. The Benker process (p. 200), which has a tendency to increase the quantity of NO, must also increase this orange vapour in the exit-gases, which, of course, is best noticed where the gases issue from the Gay-Lussac straight into the air, and not into a chimney.

Crowder [2] gives a table of averages of the amount of acids contained in the gases both on entering and on leaving the Gay-Lussac tower. The gases on entering contain from 3 to 4 gr. of acid per cubic foot, calculated as SO_3 (but in reality consisting of sulphur dioxide, sulphuric acid, in the form of mist, and nitrogen acids), and on leaving only about 1 or 2 gr. He believes that, if the gases contain more than this quantity, it indicates that sulphur dioxide has penetrated into the absorbing-tower, the result being a reduction of nitrous acid and loss of nitre. On principle this is, of course, correct, but it is not certain whether the above amount is the real limit in all ordinary cases. Crowder also noticed that the proportion of oxygen in the gases issuing from the tower is always slightly greater (0·08 to 0·54 per cent.) than in the gases passing in. The explanation of this phenomenon proposed by him, viz., the diminution of volume consequent upon the removal of SO_2 or some decomposition of the oxides of nitrogen, is altogether

[1] *Loc. cit.*, p. 313.
[2] *J. Soc. Chem. Ind.*, 1891, p. 303.

inadmissible ; any chemical action of the SO_2 and the nitrogen oxides within the Gay-Lussac tower could only tend to diminish, not to increase, the amount of oxygen, and the shrinkage caused by the removal of those gases is far too slight to be observed in gas-analysis (it is, of course, useless to expect such gas-tests to give accurate results, even in the first decimal per cent.). Lunge suggests that Crowder's observation was due to some air being drawn into the exit-tube by a slight leak or by the feeding-holes sucking in a little air ; this is extremely probable, as the Gay-Lussac tower usually offers great resistance to the draught, and the inward suction at the exit-tube, as shown by an air-gauge, is consequently many times greater than that at the inlet-tube.

Attempts have been made to absorb or utilise the last traces of acids in the exit-gases. Sometimes they are washed with water in a small coke-tower or plate-column. Up to the present, however, these attempts have not proved successful.

Mitarnowski and Benker (Fr. P. 212989) propose passing these gases through a solution of ferric sulphate, or through a column charged with granulated copper and fed with water, in order to produce sulphate of copper ; but this will hardly pay, for the same reason as that which is at the bottom of the necessarily incomplete action of the Gay-Lussac tower.

Taraud and Truchot (Fr. P. 425913 ; B. P. 16866 of 1910) wash the chamber exit-gases in one or two towers by water (introducing air or oxygen if necessary), and return the weak sulphuric acid formed to the chambers as a spray. Then follows an alkaline washing and the liquids formed here are also returned to the chambers.

The same inventors (Fr. P. 431427) wash the gases leaving the Gay-Lussac tower by an acid solution of a ferrous salt, decompose the compounds of NO and ferrous sulphate formed in this way by heating the solution, and reintroduce the NO into the chambers.

According to their B. P. 9461 of 1911 ; U.S. P. 1068021 ; Ger. P. 268815, they first remove the sulphur acids from the gases passing out of the Gay-Lussac tower by treating them with alkaline-earth carbonate in lumps, and then absorb the nitrous gases by solutions of caustic or carbonated alkali, with formation of sodium nitrate and nitrite. This treatment takes place

in towers or scrubbers, which are either left empty (in which case the alkaline liquids are introduced in the form of spray) or filled with packing materials. Air is injected into the first tower in order to oxidise the NO. The solutions of nitrate and nitrite obtained are sprayed into the vitriol chambers. According to their Ger. P. 277324, the sulphuric acid carried away is retained by washing with water, instead of alkaline earths.

According to their B. P. 16611 of 1912, the washing with alkali may be left out if the washing with water has been well carried out.

Laufer (Fr. P. 480247 of 1915) treats the gases leaving the Gay-Lussac tower with water-sprays or the like, for the purpose of absorbing the acid fumes, and the water containing the recovered products is reintroduced into the process.

Various Plans for recovering the Nitre.

Merely for the sake of completeness, it may be mentioned that several other plans have been proposed for utilising the nitre-gas escaping from the chambers. Not one of these has ever possessed any practical value, and they can hardly be said to have even an historical interest, since they have never been employed except in a few isolated cases.

Kuhlmann, for instance, employed thirty Woulfe's bottles, the first ten of which were filled with water, the second ten with a solution of barium nitrate, and the third ten with barium carbonate suspended in water. The mixture produced in the last ten bottles was used in the second ten bottles, where barium sulphate ("permanent white" or "blanc fixe") was precipitated. Others have used milk of lime, ammoniacal liquor, or even pure water for the absorption of the acid vapours. All these plans are so very much less advantageous or complete than Gay-Lussac's process that they cannot compete with it.

The Badische Anilin- und Sodafabrik (Ger. P. 238369) absorb these compounds by a mixture of nitrates and nitrites, thereby obtaining pure nitrates.

Their further patents (Ger. Ps. 233967 and 233982; Fr. P. 412788) absorb the nitrous gases by bases suspended in a finely divided form, without towers.

Mechanical washers for the recovery of nitrous gases leaving the last chamber, according to the *Alkali Inspectors' Report* for 1915,[1] have been successfully introduced in one works, and were on the eve of introduction into others. They have the advantage over Gay-Lussac towers in that there is no blockage possible.

Denitration of the Nitrous Vitriol.

The operation going on in the Gay-Lussac towers, where the final result is the production of an acid more or less charged with nitrous compounds, viz., the nitrous acid, requires as its necessary complement another operation, by which the nitrous vitriol, which by itself has no practical use, can be reintroduced into the chamber-process. This is done in order that the absorbed nitrous compounds may be restored, and that the sulphuric acid originally employed may be recovered. The invention of the *Glover tower* must be regarded as almost equally important as that of the Gay-Lussac tower; and in fact the *general* introduction of the latter only dates from the time when manufacturers were able to combine its use with the Glover tower.

The various contrivances for denitrating nitrous vitriol were described and criticised thoroughly and in detail by Fr. Bode, in 1876, in a paper *On the Glover Tower*, which obtained the great prize of the Berlin Society for the Promotion of Industry. This essay has been used to some extent in the following description. Bode's paper has also been published in *Dingl. polyt. J.*, vols. ccxxiii. to ccxxv.

The methods for denitrating nitrous vitriol are founded, on the one hand, on the effect of diluting it either with hot water or steam, or with a combination of both, and, on the other hand, on the action of sulphur dioxide, mostly combined with a certain amount of dilution. It has been proved in detail by theoretical investigations that the nitrososulphuric acid is completely decomposed, either by the dilution or the action of the sulphurous acid. The apparatus and modes of procedure employed in practice for denitration will now be described.

[1] Quoted from *Chem. Trade J.*, 1916, p. 284.

By Steam or Hot Water.

One of the oldest apparatus for denitration by steam was described in Payen's *Chimie industrielle*, and has been copied from this into most text-books. It may be called the "shelf-apparatus," and as it is on the principle of the well-known "Coffey still," it need not be described here.

Another apparatus, constructed on the same principle, is the "Dénitrificateur" proposed by Gay-Lussac himself. It is a lead column of square or circular section, provided with a grating a little above the bottom, and packed with coke on the top of this. The nitrous acid runs in at the top, being sprayed by means of a rose. The gas from the sulphur- or pyrites-burners enters below the grating and meets the descending nitrous vitriol; at the same time, either a jet of steam is introduced separately, or the gas is previously conducted through tanks filled with water, in order to saturate it with moisture.

In these apparatus the denitration evidently takes place by the joint action of the steam and the sulphur dioxide. The acid ought to arrive at the bottom free from nitrogen compounds; but it is then so dilute that it must be run back into the chambers. Apparatus of this type are not to be found in use anywhere at present, for good reasons. Since the acid in them is diluted to the same extent as in the process of denitrating by hot water or steam alone, they present no advantage over the latter; indeed they were in the first instance replaced by the latter processes. They have this drawback also, that they last a very short time, on account of the rapid destruction of the lead. The destructive action is always very strong in the first chambers, which, even under the best conditions, and in the presence of a Glover tower, suffer more than the remaining chambers, and have to be made of thicker lead if they are to last as long. This is due partly to the heat of the gas, partly to the nitrous compounds themselves. It is evident that much more of this action must take place in a very small chamber, such as the "shelf-apparatus" or "Dénitrificateur." The worst, however, of these apparatus is that the steam introduced into them necessarily leads to the condensation of very dilute sulphuric acid and nitric acid on

the sides of the apparatus, which must rapidly corrode the lead. Moreover, considering the small size of the chambers serving as shelf-apparatus or *dénitrificateurs*, any changes in the chamber-process, in the composition of the kiln-gas, in the supply of steam, in the outer temperature, etc., must be felt in them very much more than in a large lead-chamber. Therefore, from time to time, stronger nitrous vitriol will condense on the walls, and be diluted directly after by an increased condensation of water, and thus become charged with nitric acid. The inside of the walls of a working lead-chamber is always covered with a white slimy lining of lead sulphate, which retains acid like a sponge, but at the same time protects the lead from further action, until the acid is diluted by condensed steam, when gas is given off from it, and the slimy mass of lead sulphate is loosened and washed off, whereupon the lead is again exposed to fresh attacks. The older denitrating-apparatus, therefore, were exposed to very rapid destruction, because they employed the simultaneous action of sulphur dioxide and of steam, and were soon abandoned.

In England, most manufacturers later on *diluted the nitrous vitriol* in separate small *boxes with water and steam*, whilst on the Continent usually "steam-columns" or "cascades" were preferred.

The *denitration by steam alone*, or by steam with very little water, takes place in the so-called *steam-column*. It consists of a cylinder of strong sheet-lead 11 ft. 6 in. high and 3 ft. wide, lined with acid-proof bricks. The bottom is formed by a lead plate (or better a loose saucer), and the top by a stoneware slab. The column is filled with bits of flint nearly up to its cover. The flints are about the size of a fist near the bottom, and decrease towards the top to the size of a walnut. In place of these, some works use bits of broken stoneware. The nitrous vitriol running in at the top trickles down through the packing, and is decomposed by the rising steam. Whilst the nitrous acid given off from it goes into the chamber in the state of vapour, the sulphuric acid, diluted by the condensed water, arrives at the bottom of the column, and runs into a tank.

Very many investigations have recently been made upon the denitration of acids from explosives factories, and the

apparatus has been fully described in the technical press, to which the reader is referred.

Steam-columns are also made without a lead jacket, but they cannot in this case be built up of bricks but must be made of Volvic lava.

J. A. Beck (B. P. 28743 of 1913) replaces the Glover tower by a column very similar to the gas washer. The units comprising the column have a central upstanding pipe covered by a hood having an open or perforated lower end.

The acid is supplied at the top of the column, and the gas enters the lowest chamber by an inlet and bubbles through the liquid in the successive chambers to an outlet at the top.

A column of this description may also be used in place of the usual Gay-Lussac tower.

THE GLOVER TOWER.

The apparatus which is now used for denitration in nearly all vitriol works is the *Glover tower*, and although its inventor had, in the first instance, constructed it for denitration, it might just as well be described as a cooling and a concentrating apparatus. The Glover tower was invented by the late John Glover of Wallsend, and he built his first tower in 1859 at the Washington Chemical Works, near Durham. This tower was made of fire-bricks and packed with a network of thin fire-tiles. It lasted a year and a half, and proved the correctness of the principle. In 1861 Glover, at the same place, built a lead tower. When erecting another works at Wallsend in the same year, he, of course, built a similar tower there also, which worked until 1863 or 1864. From the experience gained in this way Glover constructed in 1864 a third tower, which in all essential respects was the same as is used to this day. Up to that time only his nearest neighbours had introduced the tower. It must here be observed that its inventor had not only taken out no patent for it, but, with great liberality, had shown it to every one interested in the matter. In spite of this, some of the manufacturers on the Tyne, intending to "improve" the tower, made mistakes in its construction; and, at least in one case, this led to its being given up, although it has since been reintroduced. Between 1868 and 1870 all the

larger and better-managed works on the Tyne introduced the Glover tower. It was adopted in Lancashire about 1868, and in London in 1870. Until 1871 nothing had been published about it.

Lunge, in his fourth edition, pp. 854-856, discusses the functions of the Glover tower and gives the opinions of Kuhlmann, Vorster, and others in relation to the alleged loss of nitre by the use of this apparatus. His own conclusion is, that there is practically no loss, and this has been proved by long practice.

Functions of the Glover Tower.—Although outwardly resembling a Gay-Lussac tower, the function of the Glover tower is exactly the opposite—viz., to deprive the nitrous vitriol running off *at the bottom* of the Gay-Lussac tower of its nitrous compounds, and to restore it to a proper state of concentration for applying it again *at the top* of that tower. This, certainly, is only one of the functions of the Glover tower, but the most important and characteristic of all. The tower fulfils this function by exposing the nitrous vitriol, usually mixed with chamber-acid, in a finely divided form, to the action of the hot burner-gas. The heat of this concentrates the sulphuric acid, and the sulphur dioxide denitrates the nitrosulphuric acid. The simultaneous concentration and action of the sulphur dioxide seem very much to advance the denitration, which takes place according to the equation :

$$2SO_2(OH)(ONO) + SO_2 + 2H_2O = 3H_2SO_4 + 2NO.$$

Glover's apparatus cannot be compared with the apparatus described above (p. 207 *et seq.*), because in it no condensation of dilute sulphuric acid containing nitric acid can take place on the lead walls, and because it is so constructed that the lead does not come into contact with the hot gas and the nitrous vitriol. Once properly built, it continues working for many years, and causes no interruption of the process. It also possesses two very great advantages. The first is, that it is both the most complete and the most rational of all cooling contrivances for the burner-gas : the most complete, because the gas is brought into immediate contact with the cooling-liquid in the form of a fine spray, not separated from it by a metallic wall or only exposed to the cooling-action at the

circumference of the current; the most rational, because no expense has to be incurred for pumping up cold water for cooling, and the steam generated is at once usefully employed in the chamber. The second and still greater advantage of the Glover tower is, that in it not only all the acid serving for absorption in the Gay-Lussac tower, but the whole of the chamber-acid is brought to 144° or even up to 152° Tw. without any expense except that of pumping the acid to the top of the tower—an expense which is very small indeed, especially where the exhaust-steam of the air-pumping engine is used as steam for the chambers (*cf. supra*, p. 105).

The Glover tower can, moreover, be used for introducing the requisite fresh nitric acid into the chambers without any special apparatus, by running it down together with the nitrous vitriol. Before it arrives at the bottom it is fully denitrated, as well as the nitrous vitriol itself (*cf. supra*, p. 208).

Construction of a Glover Tower.

In the construction of a Glover tower the guiding principle is to provide an apparatus perfectly tight against liquids and gases, and at the same time capable of resisting both heat and the action of strong acids in the liquid and gaseous form. A gas-tight apparatus is preferably made of some metal, and this principle is followed in the construction of vitriol-chambers. But lead, the only metal to be thought of, does not resist the action of hot acid-gases at temperatures not very far removed from its melting-point. Acid-proof material of any other kind requires joint-making with some mortar or cement, none of which again is sufficiently resistant in this case. The solution of the difficulty is attained in this way:—An outer shell of lead, constructed as usual in the case of chambers, towers, and the like, is provided with an acid-proof stone or brick lining, *without any mortar*. The latter, which would be destroyed directly, is not necessary for the stability of the erection if it is properly designed, nor need the lining be gas-tight, as the small amount of gas which finds its way through the joints is then sufficiently cooled down to render it harmless Nor can the lining itself, which is always a bad conductor of heat, transmit enough heat to be dangerous to the lead.

The lining is the next thing to consider. Undoubtedly the best material for this purpose is *Volvic lava* (see p. 193), which resists both acids and heat better than any other material so far known. It occurs near Clermont-Ferrand, in France, and can be had in large blocks which are easily shaped to design, *e.g.* from Brosson Lafilichat frères, or from A. Moity, both of Volvic (Puy-de-Dôme).

Next to this, where Volvic lava is considered too dear or difficult to procure, comes "chemical" brick or stoneware, *i.e.* such as resists the acids and also the heat up to the required extent, but it need not be "fire-brick" proper. These bricks always yield some alumina to the acid, but they may serve for several years.

In Great Britain the "blue bricks" of Mold in Flintshire are usually employed for lining Glover towers. The following is the composition of the class, called "Metalline," supplied by the Buckley Brick and Tile Company, and that supplied by Davison & Co., Ltd., sold under the name of "Obsidianite":—

	Metalline.[1]		Obsidianite.
	1884.	1902.	
Silica	63·01	54·97	79·10
Alumina	25·95	34·36	15·20
Iron oxide	6·49	6·44	3·50
Lime	0·83	0·55	1·20
Magnesia	0·40	0·49	0·30
Manganese oxide	0·75	trace	...
Alkalis (Na_2O; K_2O)	2·57	3·24	trace
Organic matter and loss	0·09	...	0·70
	100·09	100·05	100·0

The "packing" of the Glover tower is made of similar material to the lining, and is described at the end of this chapter. The principles of constructing the various parts of the Glover tower will now be explained.

The *foundation* of the Glover may be constructed exactly as described under Gay-Lussacs (p. 148), and the framework also. The top of the foundation is covered by a lead apron

[1] The small difference between analysis of 1884 and that of 1902 shows uniformity of quality.

6 or 7 lb. to the square foot, for the purpose of protecting it against acid drippings. This apron may be turned up so as to form a saucer with an overflow spout; and if this be kept full of water it will help to preserve the inner saucer, by keeping this at a moderate temperature.

Sometimes the platform at the top of the foundation is covered with a molten mixture of pitch and brimstone, and the leaden apron is put upon this while still warm. This is an absolute protection against any corrosion of the iron pillars and girders by any acid finding its way down.

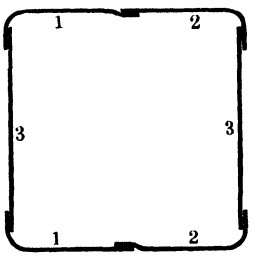

FIG. 110.

In the case of Glover towers of square section, the lead lining is usually made of 36-lb. lead half-way up, the remaining portion of 14-lb.

(Some acid-makers prefer obtaining the lead sheets tapering in thickness from 14 lb. to 36 lb.)

Its sides are suspended from the top and side joists, just like those of a chamber. The lead stands a little off the wood, which is of more importance for the protection of both the wood and the lead. In order to avoid seams at the corners, where they would be weakest and where they could not be very well repaired on account of the frame, two of the sides are made of two sheets of lead (1, 2, Fig. 110) each, which are burnt together in the middle, and which reach round the corners, where the sheets 3 are burnt to them. The seams are best burnt inside. All the side sheets reach down from the top to the bottom without any horizontal seams, and hang loosely within the saucer.

The bottom saucer is formed of two sheets of lead burnt together in the middle and turned up all round to a height of 12 in. Since sheets $\frac{1}{2}$ in. thick cannot be burnt together in the usual way, they are joined as follows. They are placed close together, after having the edges cut off slantingly and scraped clean (Fig. 111). Into the rebate *a*, thus formed, lead heated above its melting-point is poured. The molten lead, before solidifying, fuses the margins of *a*, and this is further assisted by a red-hot iron, so that the whole unites into a solid mass.

Another method of joining such thick sheets of lead is to cut the lead as shown in Fig. 111. The borders are then heated with a hot iron, and the blowpipe is applied at once so that the lead at this place melts for a certain depth and runs to the bottom of the triangular channel between the two sheets and closes this up. The whole channel is then filled up by heating, with the blowpipe, both the borders and a thick strip of lead, as when burning horizontal lead seams (p. 11).

Sometimes, as is seen above, the bottom of the tower stands in another saucer, filled with water, which is allowed to get hot, but even then forms a protection to the inner saucer against overheating. In other cases there is a constant flow of cold water round the bottom saucer, so that the acid gets cooled to some extent before running away, which is an additional advantage. Another plan for cooling the bottom is by arranging

FIG. 111.

a network of air-channels in the brickwork underneath the lead bottom.

The tower bottom is protected inside by a layer of 3-in. acid-proof slabs. Sometimes a piece of lead is laid loosely on the bottom before putting the slabs on.

The "*lip*," where the lead side of the saucer is turned over to form a place for the acid to run off continually into a leaden spout, is important. This part, over which hot acid is incessantly running, and which cannot remain covered by a protecting layer of lead sulphate, is exposed to very great wear and tear. As it cannot well be repaired while the tower is at work, the plumber must not neglect to put a false lip, consisting of a piece of a half pipe of silica or earthenware.

An excellent arrangement for avoiding wear and tear of the saucer is to provide an earthenware or silica pipe A, about 3 in. diameter, Fig. 112. The hot acid is thus conveyed from the inside of the tower and the saucer remains comparatively cool.

The joint B is made of suitable acid-resisting cement or molten lead, and the pipe A can at any time be replaced without stopping the process, the plumber making use of

temporary syphons in order to maintain the acid at a low level whilst he makes the repair.

The lead top of the tower is suspended from wooden or iron rails, to which it is fastened by straps, and which are supported by the side frame. Towards the centre it is dished out so that any acid leaking from the tanks cannot run down the sides of the tower, but finds its way into the tower through a hydraulic lute.

The *inlet and outlet for the gases* require special care. About the outlet-pipe nothing need be said, except that on its bottom

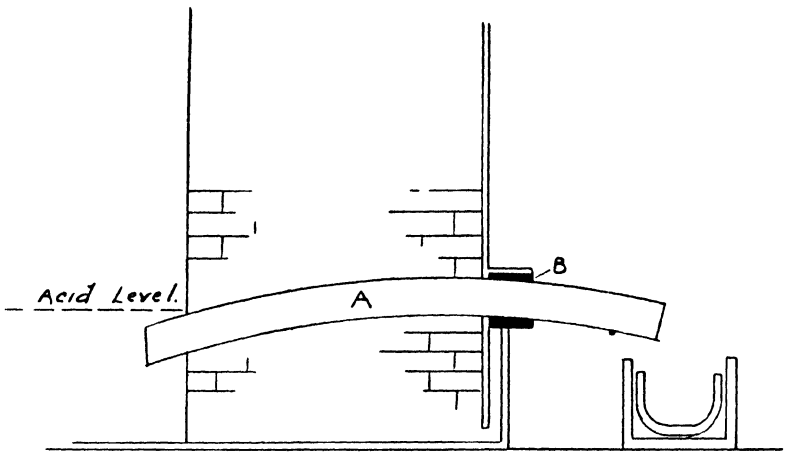

FIG. 112.

a small ledge is formed, which compels any acid to run back into the tower; or the pipe rises a little towards the chamber. On the other hand, the fixing of the entrance-pipe, which ought to have a slight fall towards the tower, is not quite such a simple matter, and at first caused much difficulty. It is made generally of cast-iron, and has, in the great majority of acid-works, a temperature of at least 300°.

Fig. 113 represents an arrangement used by the writer for many years which was found very satisfactory. The burner-gas stack *a* may be either constructed of brickwork as shown, or of cast-iron pipes. In case of brickwork being used, it should be constructed with a lining of acid-resisting bricks, and the whole firmly held together with iron brackets and tie-rods. Upon this rests the branch-pipe *b*, one and a quarter

inches thick, with manholes and lids as shown for facilitating cleaning.

Attached to the branch is a short pipe *c*, with the flange cast on at a slight angle, so as to allow any condensed acid to flow into the tower. This pipe is preferably lined with

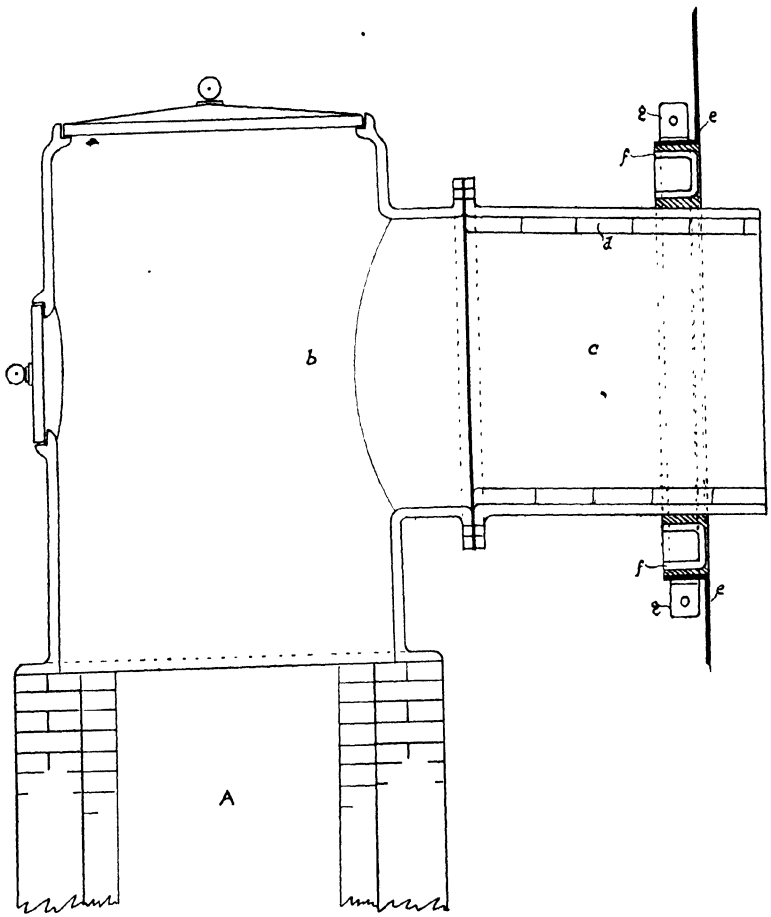

FIG. 113.

specially shaped acid-resisting brickwork *d*. In the side of the tower at the place in question a circular hole is cut, to the circumference of which an upstanding flange *e* is burned, slightly larger than the outer circumference of the collar mentioned below.

Before placing the burner-pipe into this opening, an annular cast-iron collar *f* is put on, and the joints of this to the Glover tower and burner-pipe are made with a cement of tar and china clay, and the two joints tightened up by means of the iron straps *g* in halves. For the purpose of protecting the lead work from excessive heat, the collar may be enclosed and water circulated through the annular space.

At some works the burner-gas is carried into the tower by pipes, made of Volvic lava, in two halves, as shown in Fig. 114. In this case no special contrivance is required for protecting the lead at the joint.

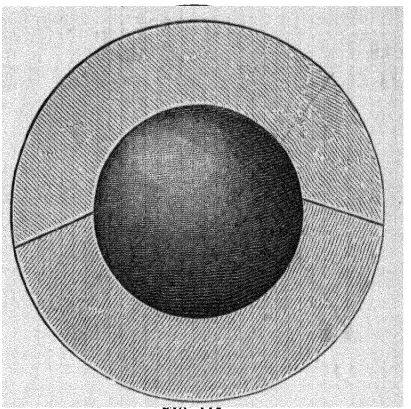

FIG. 114.

The *lining* of the tower is made of the materials described above (p. 212), and is constructed so as to serve at the same time as a support for the packing.

The whole lining of the tower as well as the arch of the grid must be walled *dry*, without mortar of any kind. In order to make the arch sufficiently stable without mortar, it should be made of large blocks *a*, Fig. 115, which also shows the packing *b* of bricks of the ordinary size. In some works all the bricks of the lining are ground one upon another, so that only extremely small joints remain. This is most easily done where the lining consists only of a few large blocks of Volvic lava (see p. 193, and below).

It is considered satisfactory if the lining of a Glover tower stands for six years without having to be renewed; sometimes it stands much longer.

Steuber & Co. (Ger. P. 227283) construct acid-towers without any lead shell, with double sides of acid-proof stones. They protect the foundation against the action of acid penetrating there by means of channels through which fresh water is constantly running (*cf.* also the linings described *supra*, p. 212).

Height of the Glover Tower.—In some cases it is preferred not to fill the tower to its very top, viz., if the gas is thus cooled too

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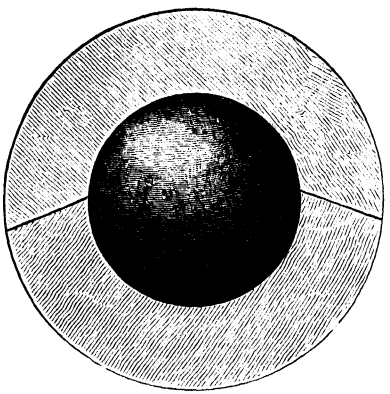

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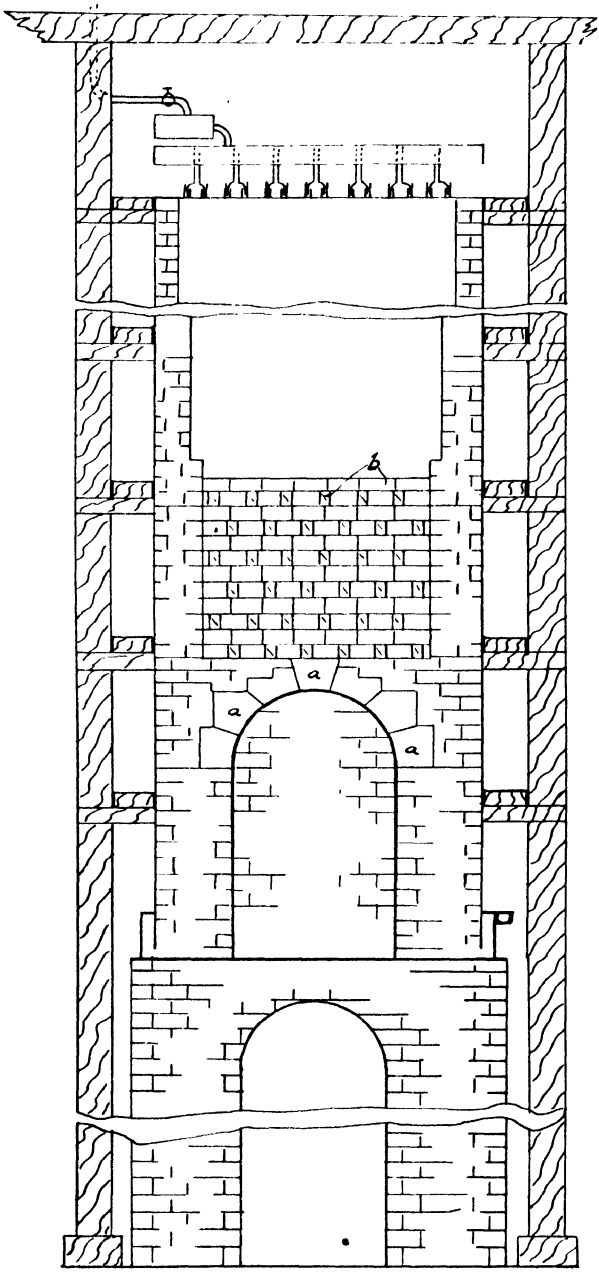


FIG. 115.

much; for then part of the first-formed aqueous vapour might be condensed again to the liquid state, dilution thus counteracting the concentration. The temperature of the outgoing gas is generally about 60°. Some manufacturers prefer from 60° to 75°. If too much cooling must be avoided by leaving the upper part of the tower empty, that portion might be left out altogether and the tower be made so much shorter. In fact, towers from 18 to 20 ft. high have recently been preferred to high ones. The height will, of course, depend upon the temperature of the gas when entering the tower, and therefore upon the kind of ore burnt, upon the presence of dust-chambers, upon the length of the flue from the pyrites-burners to the tower, and so forth. The proper height for a Glover tower, under ordinary circumstances, is from 20 to 25 ft. At one works, where two towers were erected, one 24 ft., the other 36 ft. high, it was found that the higher tower did no more work than the lower, so that the expense caused by the additional height, both in erecting and packing, seems to have been useless.

The Cubical Contents of the Glover Tower.—For a daily consumption of 10 tons of pyrites containing 48 per cent. of sulphur, a tower 10 ft. square by 25 ft. high is sufficient. This for every ton of sulphur consumed amounts to 520 cub. ft. Where two towers are used, each having a set of burners feeding one chamber (the first of a series), the writer uses two Glovers measuring 8 ft. square by 20 ft. high, which equals 550 cub. ft. per ton of sulphur per twenty-four hours. All the above measurements are taken inside the lead work.

It is the American practice to state the capacity of the Glover tower in terms of cub. ft. of nett packed volume per ton of acid of 60° Bé., and much smaller towers are in use than is usual in this country for the same consumption of sulphur.

Instead of the square section at first universally used in constructing Glover towers, latterly, circular towers have come into use at many works (see Figs. 85 and 86). In France, the towers are usually lined with large blocks of Volvic lava, circular in section, and forming by themselves a substantial tower, although, of course, without any mortar, so that the lead shell is quite independent of them.

Circular Glover towers, even of very large dimensions, can be built without the applications of wooden or iron frames,

the lead being stiffened by circular iron hoops (covered with lead) for each 5 ft. of their height.

The advantage claimed for circular Glover towers is that they require less lead for a given cubic space, and that the lead suffers less than when it is bent in sharp corners.

Benker (1902) has built circular Glover towers of Volvic lava with a leaden shell, also towers without a leaden shell, which are cheaper and simpler to make. The towers are placed on such high foundations that the pipe from the dust-chamber has a rise towards the tower, and can be easily cleaned out. The grate is also made of Volvic stone as well as the packing, which is employed in pieces up to 6 to 9 in. These towers are never stopped up with mud.

Guttmann[1] reports that in England, too, Volvic lava towers are now made to stand by themselves, but sometimes an outer shell of 6-lb. lead is added to prevent the escape of fumes. Iron hoops covered with lead hold the lava segments together, and sometimes even these are dispensed with. No wooden structure is required, since even reservoirs are dispensed with where automatic feeding apparatus is used.

Lüty gives a design of cylindrical Glover towers[2] 10 ft. wide. The bottom is protected by a double layer of acid-proof tiles. The sides are lined up to the lower side of the grate with arch-bricks, closely touching the lead, and leaving a clear space of 7 ft. 6 in. Into this lining the inlet-pipe is built, consisting of four large moulded pieces, with an inside diameter of 3 ft. 3 in. Into this another acid-proof pipe is introduced which on the outside is connected with the cast-iron gas-pipe. On the floor two columns are placed, 8 in. square and 4 ft. 6 in. high. These, as well as the side linings, carry a grid, consisting of slabs 5 in. thick and 19 in. high, with intervals of 6·4 in., fixed by stone cubes put between the slabs. The packing begins above the grid with two layers of bricks, 13·4 × 3·14 × 7·87 in., the second layer crossing the slabs. Now follow two layers of bricks, 10 × 2 × 5·36 in., placed on edge. The lining behind the grid, and up to a total height of 21 ft. above the floor, consists of bricks shaped to the curve of the tower, 10 in. thick; above this to the top

[1] *J. Soc. Chem. Ind.*, 1908, p. 667.
[2] *Z. angew. Chem.*, 1896, p. 640.

of the tower the lining is only 5·5 in. thick. The space above the grid up to the height of the outlet-pipe is filled with the cylinders described on p. 242, placed regularly in layers with broken joints.

Later[1] Lüty gives further details respecting Glover towers, especially advocating the erection of two towers acting in parallel and dividing the gas from the burners. This was more particularly advocated by Niedenführ,[2] who also recommends a special kind of tile for packing the towers which avoids the drawbacks mentioned by Lüty. The employment of two parallel towers was subsequently abandoned, owing to the difficulty of an exact division of the gases, except for cases where two sets of burners each have their own Glover tower, both connected with the same set of chambers.

The distribution of the acid for feeding the Glover tower is effected precisely as in the case of the Gay-Lussac tower.

For large Glover towers it is preferable to employ several troughs, running right across the top of the tower, with a number of lips on either side, each connected with a pipe leading to a hydraulic lute on the top of the tower.

The regulation of the flow for the Glover tower is nearly always effected by hand, or else by the apparatus shown on p. 167. Any apparatus for an absolutely constant supply of liquid would be out of place here, as the relative quantities of nitrous vitriol and chamber-acid vary, and must be regulated according to the state of concentration and denitration of the outflowing acid.

Position of the Glover Tower.

At most works, the Gay-Lussac and Glover towers are erected side by side, so that their tops are accessible by a common staircase, and are even on the same level (in which case the Glover towers, being much shorter, must stand on a higher foundation than the Gay-Lussac towers). It is unnecessary to point out how much the supervision of the work, the feeding of the towers, etc., is simplified by this plan. There is also an advantage that the nitrous vitriol has not to run very

[1] *Z. angew. Chem.*, 1897, p. 490.
[2] *Chem. Zeit.*, 1897, p. 664.

far, as it sometimes contains gas (NO) which impedes its free running.

Working of the Glover Tower.

The Glover tower may be operated with only the nitrous vitriol running down, without any chamber-acid ; but in that case it does not deprive the acid of all the nitrous compounds, but of the principal part only (down to about 0·2 per cent. of N_2O_3), and at the same time concentrates it to over 150° Tw. This acid is now used again in the Gay-Lussac tower for absorption, and thus a circulation of acid takes place between the two towers. There is always a certain addition to the acid, as free sulphuric acid is formed within the Glover tower.

However, the Glover tower is not usually fed with nitrous vitriol alone, except in the case of temporary disturbances. The apparatus is generally arranged so as to be fed with a mixture of *nitrous vitriol* (or fresh *nitric acid*) and *chamber-acid*, in which case not only is the denitration completed, owing to the initial dilution, but a very desirable secondary effect is obtained, viz., the concentration of the chamber-acid, and the abstraction of the minute proportion of nitre which it generally contains. If the acid produced in the chambers is only 106° Tw., it can still be concentrated to 144° without any difficulty in the Glover tower, even when the gas comes from a burner for pyrites-smalls and is therefore somewhat cooled in dust-chambers. That the denitration by sulphur dioxide becomes more perfect by dilution follows from the researches of R. Weber, Cl. Winkler, and Lunge.

Where the chambers make very strong acid, which does not sufficiently dilute the nitrous vitriol, a little water should be run down at the same time.

The stream of nitrous vitriol and that of chamber-acid are regulated entirely according to the degree of denitration and of concentration shown by the acid running off at the bottom of the Glover tower. The more chamber-acid is run through (that is to say, the greater the dilution), the better the denitration ; the less chamber-acid is used, the more concentrated the acid. There is, however, no difficulty in attaining *both* objects, viz., to get an acid completely denitrated and yet

testing 148° Tw., if good pyrites be burnt, and if the burner-gas be employed as hot as possible by placing the tower close to the burners. In the case of poor ores or of smalls-burners with large dust-chambers, the denitrating action will also be complete, but the concentration cannot always be carried so far.

It was at one time assumed that the chamber and nitrous acids should only be mixed inside the tower in order to avoid loss of nitric oxide, but this has not been found necessary, and it is now usual to feed them together, thus greatly simplifying the distributing arrangements.

According to the *Rapport du Jury International* (Paris, 1891, p. 5), experiments made in one of the factories of the Société St. Gobain have shown that the denitration of the nitrous vitriol in the Glover tower is almost instantaneous; even at 3 ft. 3 in. below the exit-pipe it had proceeded to its maximum. It would be wrong, however, to ascribe general validity to that observation. The result quoted is probably only attained with greatly diluted acid and very hot gases. Although no doubt the principal denitrating work is done in the top part of the tower, a *complete* denitration will require a depth of 10 ft. or upwards, apart from the requirements for performing the concentrating work.

For the denitration of *poor* gases, *e.g.* those produced in the roasting of lead ores, the Aktien-Gesellschaft für Bergbau, Blei- und Zinkfabrikation (Ger. P. 253493) supply the Glover tower with stronger gases, especially those obtained by roasting zinc-blende, iron pyrites, copper pyrites, etc., and mix the acid gases formed thereby with the dilute SO_2 gases to be oxidised.

Hegeler and Heinz (Fr. P. 341257) work the Glover tower in such a manner that it acts as a *producer of sulphuric acid from top to bottom.* As it furnishes hot concentrated acid, they protect the sides of the tower against attack by lowering the temperature of the bottom part. For this purpose they inject part of the nitrous gases into the burner-gases by means of a fan, before entering the Glover tower. They assert that in this way they get the Glover acid up to 168° Tw. The same inventors (Ger. P. 184959) introduce part of the gases coming out of the top of the Glover tower into the bottom, by means of a special pipe, provided with an arrangement for propelling the gases. This process is intended to give a better utilisation

of the nitrogen compounds and a reduction of the chamber-space by the more intimate mixture of the gases, and it prevents an excessive heating of the bottom part of the tower. The nitrous compounds thus pass several times through the tower and are more thoroughly utilised for the production of sulphuric acid, before they pass into the first chamber.

The acid running out of the tower is tested for its strength (which should be between sp. gr. 1·71 and 1·75); for its temperature (if it is to be immediately pumped up on to the Gay-Lussac tower); and for its content of nitrogen acids, if it contains more than traces of these, in the same way as the nitrous acid (p. 291 of Vol. I).

Glover Towers connected with Dust-burners.—One of Bode's towers, working with dust-burners, had to receive the burner-gas after passing through a large dust-chamber. The gas, therefore, reached the tower only at 152° to 180°, and the temperature on leaving it varied between 30° and 40°. The hot acid running off showed a temperature between 96° and 110°. When this tower was employed only for concentrating chamber-acid, it evaporated daily 6 tons of water and produced 2 tons 3½ cwt. acid of 144° Tw. from chamber-acid of 110° Tw. This corresponds to a saving of coal for chamber-steam equal to 1½ cwt. per diem. When the tower was employed both for concentrating and denitrating, it supplied daily on an average 2 tons of acid of 144° Tw., and evaporated 9 cwt. of water. The denitration was perfect. The kiln-gas contained 7½ per cent. by volume of sulphur dioxide. Of course, the above results are much less favourable than with the usual initial temperature of 300° to 400°. Even in the latter case the temperature of the gas leaving the tower does not exceed 50° to 60°. A tower of 8·28 sq. m. section, according to Vorster,[1] evaporated 1400 kg. of water in twenty-four hours. Another tower of 4·55 sq. m. section evaporated 1048 kg. of water, the kiln-gas containing 8 per cent. by volume of sulphur dioxide.

Even when, in Bode's Glover tower, by an accident, the percentage of the kiln-gas had gone down to 6 or 5 per cent. of sulphur dioxide, there was still complete denitration and an evaporation of 7 cwt. of water daily, equal to 1·7 ton of acid of 144° Tw. Bode concludes from this that even when calcining

[1] *Dingl. polyt. J.*, **213**, 411.

the poorest ores the Glover tower still remains a useful apparatus.

At those works where sulphuric acid is made from *brimstone*, Glover towers are not so regularly employed as with pyrites-burners. The reason for this cannot be insufficient heat of the gases, as is proved by the practice of several large works where the Glover towers work perfectly well with brimstone-burners, and show all the advantages found elsewhere. Sometimes it is asserted that the higher value of brimstone acid as against pyrites acid is impaired by iron carried into it from the Glover tower. This cannot, however, take place except with an inferior form of packing material, and it is entirely avoided by confining the work of the tower to denitrating the nitrous vitriol, and taking the sale-acid from the chambers or from the concentrating apparatus. The real reason for the comparative neglect of the Glover tower at brimstone-acid works is that many of these works are small and cheaply laid out, and are managed with insufficient care, so that their owners would rather lose nitre and sulphur than incur the expense of erecting and the trouble of working Glover towers.

At larger works, possessing a number of Glover towers, it is a frequent and convenient arrangement *to work them in different ways*, viz.; partly for making acid for the Gay-Lussac towers and partly for concentrating acid. The first should be as strong as possible, and need not be entirely denitrated; it can be obtained in this state by feeding only a small amount of chamber-acid along with the nitrous acid. There is thus a constant interchange of acids between the two kinds of towers; but the Glover tower makes a good deal of fresh acid, so that part of this acid must be employed for other purposes.

The acid for decomposing salt, or for sale, etc., should be entirely denitrated, and need not be so strong as the acid for the Gay-Lussacs. For this purpose much more chamber-acid is fed along with the nitrous vitriol.

The *various functions* which are fulfilled by the Glover tower have already been pointed out (p. 209). The object for which it was first constructed, the *denitration of the nitrous acid*, that is the recovery of the "nitre" from this and the restoration of it to the chambers, is carried out in the most perfect way and without any trouble. It is easy to work it so

that the acid at the bottom contains even a slight excess of SO_2 (which is compatible with a very slight percentage of N_2O_3), and a very high temperature is not required for it, especially when the nitrous vitriol is diluted with chamber-acid.

Lunge's statement that the fear of losing any nitre in the Glover tower by reduction to nitrous oxide or nitrogen is totally unfounded, has been fully confirmed in practice (cf. p. 210). Far less nitre is consumed in the manufacture of sulphuric acid than before the introduction of the Glover tower; and the change has in most cases been so sudden that it seems impossible to overlook this evidence.

The second principal function of the Glover tower is that of *concentrating* chamber-acid, which is intimately connected with two other functions: *cooling the gases* and *supplying part of the steam* for the chambers. The concentrating action of the Glover tower was first studied in detail by Vorster,[1] but he neglected the acid brought over with the burner-gas as SO_3 and that formed within the tower itself. Both these sources have been taken into account in the investigation of Scheurer-Kestner.[2] From his analyses of burner-gases it appeared that these contained up to 9 parts of SO_3 to 100 SO_2; the average was about 3·5 parts. As there is enough water even in the air and the pyrites to hydrate the SO_3, it is sure to be retained in the Glover tower. He further shows the mistakes committed by Vorster in his calculations, from which the latter had concluded that very little new acid was formed in the tower; and he opposes to this, not merely the practical experience, according to which the introduction of a Glover tower saves from 10 to 20 per cent. of chamber-space, but also some special large-scale experiments made with an actual tower at the Thann acid-works, by carefully measuring for some weeks the excess of acid coming out from the tower over that going in. Thus it was found that the Glover towers made 15·7 to 16·3 per cent. of all the acid produced in the manufacturing apparatus. To this should be added the acid volatilised or mechanically carried away from the towers into the chambers, which was (only partially) estimated by measuring that which condensed in the connecting-pipes, and which

[1] *Dingl. polyt. J.*, 213, 413.
[2] *Bull. Soc. Chem.*, 44, 98.

amounted to 2 or $2\frac{1}{2}$ per cent. of the total make, bringing the action of the towers to 17 or 19 per cent. This was entirely proved by the result of prolonged working on the large scale, for the same set of chambers which had previously made 6 tons of O.V. in twenty-four hours, made 7·28 tons, or 17·5 per cent. more, after adding a Glover tower to the apparatus.

Lunge in his fourth edition, pp. 897-899, gives his theory of the formation of acid in the Glover tower, and concludes as follows:

"We may draw an important inference from the established facts. The usual allowance of chamber-space per lb. of sulphur burnt in twenty-four hours is 20 cub. ft., or 44,800 cub. ft. per ton of sulphur. Of this ton, one-fifth is oxidised to sulphuric acid in the Glover tower, leaving four-fifths for the chambers. This means that 50 cub. ft. of active Glover-tower space, as defined above, make acid from 0·2 ton of sulphur, or 1 ton of sulphur here requires 250 cub. ft., whilst 44,800 cub. ft. of chamber-space make acid from 0·8 ton of sulphur, or 1 ton in this case requires 56,000 cub. ft. In other words: *the denitrating zone of the Glover tower makes more than* 200 *times more acid than an equal volume of chamber-space.* If we take a chamber-space of 16 cub. ft. per lb. of sulphur = 35,840 cub. ft. per ton, this still means 44,800 cub. ft. for the acid really made within the chambers, or only $\frac{1}{150}$ of the activity of the Glover tower."

It should now be easily understood why Lunge and others recommend replacing a large portion of the chamber space by columns acting in a similarly energetic way as Glover towers (p. 69 *et seq.*).

This enormous action of the Glover tower is explicable on the assumption that the nitric oxide set free in the lower parts of the denitrating zone, according to the equation

$$2SO_5NH + SO_2 + 2H_2O = 3SO_4H_2 + 2NO,$$

is fixed again in the upper parts by the reaction:

$$2NO + 2SO_2 + H_2O + 3O = 2SO_5NH;$$

the nitrososulphuric acid thus re-formed on descending to the lower regions is denitrated again, and the NO in this way incessantly and quickly transfers oxygen to the sulphur dioxide arriving in the form of burner-gas. This action, which of

course also takes place in the chambers, is, in the Glover tower, immensely aided by the continuous mixture of the gases and their constant shocks against surfaces wetted with nitrous vitriol. The very large amount of heat produced by the chemical reactions cannot give rise to any considerable elevation of temperature, as the heat is expended in evaporating water from the acid trickling down, and concentrating this acid, as already pointed out.

If the tower be too high, and if the top be kept too cool (which will depend upon the former), much less work than that calculated above will be done in it. In this case, there will be a considerable condensation of the steam, generated below, in the upper region of the tower; this will facilitate the denitration near the top itself, and the NO generated here will be carried over into the chamber without performing the catalytic work described above. Experience has long ago shown that Glover towers ought not to exceed a certain height (25 or at most 30 ft., *cf.* p. 217) to do the best possible work, both for evaporation and for forming new acid. Sorel, in Lunge's opinion, goes much too far in advising that the Glover towers should be kept as hot as possible, and should be fed with as concentrated an acid as possible. He looks at one side of the question only, and that decidedly the less important one, viz., that there should be as great a production of acid as possible within the Glover tower, by retaining the nitrous compounds within it a very long time. He neglects two other considerations of much greater importance: that, by his mode of conducting the process, the *denitrating* work is greatly impaired, so that the acid issuing at the bottom carries away very sensible quantities of nitre, and that, by the great heat of the gases and the concentration of the acid, the life of the tower is very much shortened. Sorel's plan interferes both with the complete denitration of the nitrous vitriol, and also with the important action of the Glover tower for bringing the chamber-acid up to the strength required for decomposing salt, etc. (say 140° to 145° Tw.), merely in order to force rather more SO_2 through the chambers than they can otherwise manage to oxidise; for this object it does not seem worth incurring these serious drawbacks.

Niedenführ (B. P. 1066, of 1904) *cools* the burner-gases

before they enter the chambers by utilising their heat for concentrating the chamber-acid, or by special purifying devices, and purifies them, especially from arsenic, etc., by passing them through washers, filters, or the like. The denitration is effected by the action of these cooled sulphurous acid gases. A pressure generator is arranged before a special denitrating device, between the denitrator and the acid-concentrating plant, in order to increase the relative efficiency of the denitrator and of the nitric acid in the chamber, and to decrease the quantity of nitric acid necessary for carrying on the reaction.

A very important improvement seems to have been effected by H. H. Niedenführ, through his Ger. P. 140825, about which Lüty reports at length in *Z. angew. Chem.*, 1905, p. 1255 *et seq.*, and which is also abstracted in *Eng. and Min. J.*, 1905, pp. 634-635. He states that it is well known to every expert that, in order to obtain the best results in acid-making, the work in the burners ought to be made independent of that in the chambers. This could not be properly done as long as the draught-producer was arranged at the end of the system; it should be placed between the burners and the Glover tower. But a great difficulty to contend with, in this case, is the high temperature of the gases and, when burning smalls, the obstruction of the Glover tower by dust. Nor can the draught-producer be placed between the Glover and the first chamber, since the nitrous gases would speedily destroy any iron fan, and stoneware fans there are also unsuitable, as they require a higher driving-power and are very liable to breakage. When placed behind the last chamber, the fan is also gradually destroyed by the moist nitrous gases. This objection could be avoided in those cases where the last portion of the chamber-space is replaced by Lunge's plate-towers or other appliances which deprive the gas of most of its moisture, so that the fan can be placed between them and the Gay-Lussac. These towers also present the best means for removing the excess of heat, produced by the higher intensity of reaction, by means of the dilute acid which is run down the towers. The least practical way of getting rid of the heat of the reaction, according to Lüty, is to hang up cooling-pipes within the chamber (*vide* p. 55). He also does not think much of Benker's plan of passing the gases from the last chamber through a water-

cooler. The improvements previously mentioned have allowed the former normal production of lead-chambers to be increased, *i.e.* 17 to 25 cub. ft. down to 10 to 12½ cub. ft. per lb. of sulphur per twenty-four hours. This is, of course, apart from chambers combined with Lunge towers or the like. A real increase of that yield is now possible through Niedenführ's new invention, the principal feature of which is the division of the functions of the Glover apparatus between two towers, and placing the draught-producer between these. The burner-gases pass first through a concentrating Glover, in which they give up most of their heat and are purified from dust, so that they cannot do any damage to the fan which, owing to the diminution of the volume of the gases by the cooling, has hardly any more work to do than when placed behind the chambers. The purified and cooled gases are forced by the fan through the second, the denitrating Glover into the chambers, and ultimately into the Gay-Lussac tower. The acid (nitrous vitriol) from the latter serves for feeding the denitrating Glover. If the denitration of the nitrous vitriol is to be complete, a little steam is introduced, and sufficient chamber-acid or even water is added so that the strength of the acid feeding the second Glover does not exceed 1·619, or at most 1·65 sp. gr. In that case, this acid still holds nitrogen acids to the amount of about 0·2 per cent. nitric acid of sp. gr. 1·33. It is now run down the first concentrating Glover, in which it is brought up to sp. gr. 1·71 to 1·73 and deprived of the last trace of nitrogen acids, and is then employed for serving the Gay-Lussac towers.

This system, in a plant for working up 18 tons pyrites (44 per cent. S), where the dust-chambers were properly managed and a temperature of the gases of 400° to 420° was maintained before they entered the first Glover, permitted of adding considerable quantities of chamber-acid for concentration.

The following advantages accrue from this procedure. The work of the burners is made independent of that of the chambers, which may be worked with a minimum of draught without any bad influence on the burning work and on the composition of the burner-gas. Since the burners are working with uniform draught, more concentrated burner-gas can be obtained, say about 9 per cent. SO_2. The exit-gases from

the Gay-Lussac then show about 4 per cent. oxygen. The burners admit of much greater charges formerly, with uniform and very good results, say 0·5 to 1·0 per cent. S in the cinders. Niedenführ's system also admits of combining various kinds of burners, and working different forms of ore at the same time. At Roubaix, *e.g.*, he combined, for one and the same set of chambers, three sets of burners, one of which was worked with very bad blende, containing 10 per cent. lead, and the other two with pyrites, with occasional addition of galena, without any difficulty in the chamber process. Moreover, a larger number of burners can be charged and stirred up at the same time. There is no blowing-out of gas from the burners. The chambers can be worked at a higher pressure than with the old system ; the gases are thus brought into more intimate contact with one another, and the formation of sulphuric acid and its separation are hastened.

The excellent results obtained by the application of his process to various entirely different systems of chambers have led Niedenführ to apply for a patent for tower-shaped chambers, in which the gases travel from the top downwards, thus producing a more intimate mixture.

The original paper also gives sketches for a model set of chambers, as planned by Niedenführ, which is to combine all improvements and to produce sulphuric acid at a low cost.

(In the discussion following the reading of this paper, it was pointed out that already in 1877 the Freiberg factories, and later on American factories, worked with fans placed between the burners and the chambers. The novelty in Niedenführ's new system is the placing of the fans between two Glover towers, each of which has its separate function to perform.)

Niedenführ (Ger. P. 207765) proposes carrying out the separation of the denitrating and concentrating functions of the Glover in the same tower.

Ménard-Dez (Fr. P. 354073)[1] places behind the dust-chamber, first, a packed tower in which the gases are washed by sulphuric acid and cooled to a temperature not exceeding 500°. The products of the decomposition of sodium nitrate are introduced either before or behind that tower. Then

[1] *J. Soc. Chem. Ind.*, 1905, p. 1066.

follows a second packed tower in which dilute sulphuric acid is concentrated by the heat of the gases, and these are now passed through a series of cylinders, packed with copper turnings, or with an oxide copper ore. The solution of cupric sulphate formed here is withdrawn for crystallisation. From here the gases pass into ordinary lead-chambers, and finally through packed cylinders instead of a Gay-Lussac tower, where the residual nitrous compounds are converted into nitric acid by means of air and water.

The following *drawbacks* are connected with the Glover tower, the first of which is, however, only temporary, and much less felt where there is no coke-packing in the Glover, but only in the Gay-Lussac tower. This coke communicates to the acid, especially at the beginning, a *brown colour* (due to organic substances), which is quite immaterial to its technical application, but injures its sale. After a little time this ceases, and the acid running away from the Glover tower is then as clear as water.

The contamination with *iron* is permanent, and is somewhat stronger than in acid made from the same pyrites in ordinary chambers, simply because the tower at the same time serves for keeping back the flue-dust. According to Hasenclever, his Glover-tower acid contained 0·05 per cent. of iron.[1] (The writer found 0·06 per cent. when working with smalls pyrites without dust-chambers.)

Besides iron, the Glover-tower acid frequently contains considerable quantities of *alumina*, of course in proportion to the action of the acid on the lining and packing material, and also of arsenic.

The flue-dust and the sulphates of iron and alumina are often formed in such large quantities within the tower that it cannot be worked for any considerable time without being washed down occasionally by a strong jet of water. This, however, is not sufficient. The interstices get filled up with hard crusts, and the tower must be stopped for repacking, which is a very troublesome and expensive operation. It is therefore advisable to go to some extra expense in the first instance for the best obtainable lining and packing-material.

Where the Glover-tower acid is only used, apart from the

[1] *Berl. Ber.*, 1872, p. 506.

service of the Gay-Lussac tower, for decomposing salt, for manufacturing manure, and for many other purposes, its impurities are of no consequence; but it cannot be used for purposes where those impurities would be troublesome, and especially not for higher concentration to "rectified O.V.," as then hard adhering crusts of ferric sulphate are formed. Even then the use of a Glover tower need not be relinquished, but it must be either treated only as a denitrator, the heat of the burner-gases being *previously* utilised for concentrating acid, or else the acid required for the manufacture of rectified O.V. and similar purposes is taken out of the first chamber without passing it through the tower.

With Glover towers constructed on the Herreshoff system (p. 867, Lunge, 4th ed.), that is, with quartz lining and quartz packing, there is no alumina in the Glover acid, but the iron and arsenic derived from the flue-dust still remain as impurities, so that there cannot be much difference as regards the crusts formed in concentrating.

An interesting application of the Glover tower is that for *utilising the waste acids from the manufacture of certain explosives*, etc. At many works during the War, these acids were run down the Glover tower and were thereby denitrated.

Denitration by other Means.

Windus (B. P. 367 of 1882) proposes, instead of denitrating the nitrous vitriol in Glover towers, to do this by agitating it within the chambers, and promoting the disengagement of the gases by producing a vacuum. The agitation is to be produced by mechanical means, or by allowing thin jets of acid to fall into the acid at the bottom of the chamber. It is unnecessary to point out the impossibility of denitration by this procedure.

The proposal of Garroway (B. P. 1673 of 1883) to effect the denitration and concentration of the acid without a Glover tower, by means of stoneware vessels placed in the gas-flue between the burners and the first chamber, seems to offer very little prospect of success.

Der Norske Akt. f. Elektrokemisk Ind. and Halvorsen (Fr. P. 363157) dissolve nitrous vitriol in an excess of strong sulphuric acid, add a little water and an oxidiser, such as MnO_2,

PbO_2, CrO_3, or a chromate. The product is distilled in iron retorts, to obtain nitric acid, and the residue electrolysed to recover the oxidiser, thus:

$$Cr_2(SO_4)_3 + 6H_2O = 2CrO_3 + 3H_2SO_4 + 3H_2.$$

Salessky (B. P. 20131 of 1910; Ger. P. 232570; Fr. P. 419609; Swiss P. 52712) states that the denitrating process in the Glover tower is never assisted, but rather impeded, by the presence of SO_2 in the gases, since the reduction may go as far as N_2O. He therefore denitrates with air only, which is heated to about 200° and blown by a small fan into the Glover tower, which in this case does not receive the gases from the burners, and is fed with water or weak sulphuric acid. His B. P. 20131, of 1910, suggests supplying the nitrogen oxides, before they reach the chambers, with air, in an enclosed space, to such an extent that they are as much as possible oxidised into nitrogen peroxide.

Parent (Fr. P. 449035) sprays the gases leaving the last chamber into the first, or into empty towers placed between any two chambers. This process is stated to effect a higher concentration of the chamber-acid, a better circulation of the gas, a smaller consumption of nitre, and an increased production of acid.

Kirkham Hulett & Chandler, Ltd., Hersey and Blake (B. P. 18129 of 1908, and 23813 of 1911), employ a tower, separated into a number of compartments by horizontal partitions, the liquid being squirted about by revolving discs or troughs.

Packings for Gay-Lussac and other Towers.

The intending purchaser has a very large selection indeed of packing material for reaction and other towers. It is therefore important that he selects one which will fulfil the conditions necessary to secure satisfactory results.

(*a*) It should have the greatest possible surface per cubic foot packed without constricting the space for the travel of the gas.

(*b*) There should be intimate contact with the gases and liquid, avoiding any direct free passage of either.

(*c*) It should retain a quantity of absorbing or reacting liquid.

(*d*) There should be no possibility of an accumulation of deposit.

(*e*) It should be made of light material, but strong enough to avoid disintegration by the weight of the superposed mass; and

(*f*) It should be easily filled into columns of various shapes.

Of course it is essential in all towers, whatever the packing used, that the liquid should be properly distributed, for faulty distribution has caused many packings to be condemned unjustly.

The Nitrogen Products and Carbide Co., Ltd., and H. Nielsen (B. P. 26269 of 1913; Fr. P. 465937) describe a filling material for absorbing-, reaction-, mixing-, and cooling-towers, comprising three or more arms or blades radiating from a central boss. The blades may be either straight or helical, and smooth or corrugated, and the central boss may be with or without a central hole. These pieces can be made cheaply by pressing a plastic material through a die.

Raschig (B. P. 6288 of 1914; Ger. Ps. 286122 and 292622; U.S. P. 1141266)[1] packs reaction- or absorbing-towers with small cylinders which are simply dropped into the towers in an irregular manner. These cylinders are about as wide as high, from 15 to 50 mm., and about 1 mm. thickness of walls. They offer but little resistance to the gas-current, and yet compel it to frequently change its direction. One cub. ft. of tower space thus receives about 100 superficial feet of active surface. For catalytic reactions the cylinders may be made of asbestos or other acid-resisting material covered with a contact substance. According to Ludwig,[2] every cubic foot of tower space contains about 1660 Raschig rings, leaving 92 per cent. of the space free for the transit of the gases.

Mescher (Ger. P. 259764) employs spouts, arranged in turns on one or the other side of perforated plates, which force the gases or vapours to sudden changes of direction, leaving the substances condensed behind on the faces of the preceding plate.

[1] *J. Gasbeleucht.*, 1916, p. 597.
[2] *Chem. Apparatur*, 1915, p. 247.

Kubierschki (Ger. P. 259362) employs wire spirals made up into plates. In this way 32 superficial feet can be placed in 1 cub. ft. of space.

Berl and Innes (Ger. P. 263200) employ for the packing of reaction-towers, tetrahedra, made of wire netting, the sides of which are bent in towards the centre. This slight deformation prevents the tetrahedra from touching in more than two points; moreover, some liquid is retained at every curved edge, which promotes the absorbing action. Fig. 116 shows these tetrahedra. Part of the gas rushing upwards must pass through the wire-netting, and thus gets into intimate contact with the adhering liquid. Another part rises upwards at the side surfaces of the tetrahedra, and there gets into action. These bodies may be thrown into the tower without being regularly placed. They have a very slight weight, and occupy only from 1 to 3 per cent. of the tower space, whilst giving a large active surface. For Gay-Lussac and Glover towers they are made of lead-coated iron wire (preferably produced by Schoop's process of converting lead into dust); for the production of nitric acid from nitrous gases, they are made of aluminium wire.

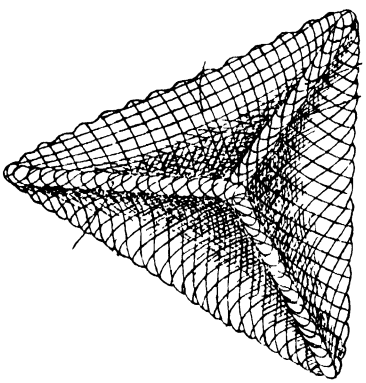


FIG. 116.

Höfling (Ger. P. 281135) packs Glover towers, etc., with pieces of tubing, provided with perforations and partitions, built up in such a way that through-going channels are avoided.

Cast silicon is employed for the purpose by F. T. Tone and the Carborundum Company.[1]

Bithell and Beck (B. P. 28743 of 1913) describe Gay-Lussac and Glover towers, consisting of several superposed parts, every one of which has a chamber with an upright tube, over which is put a cover with lateral openings. The single parts of this column are connected by pipes. The gases enter

[1] *Metall. and Chem. Eng.*, 1913, p. 103.

from below. This construction avoids the drawback of towers packed with tubes, etc., forming through-going channels which are traversed too quickly by the gases.

The Accrington Brick and Tile Co. Ltd. and S. Middleton (B. P. 8152 of 1915) furnish Glover, Gay-Lussac, and like towers with channelled packing-blocks, arranged so as to produce long, narrow, inclined passages. These earthenware blocks are easy to make, and comparatively few of them are required; they may be used in an upright or in an inverted and reversed position. If the blocks are placed end to end, and alternate blocks of each layer are reversed, or if they are laid on the top of one another, while the alternate blocks are reversed, a wall-like tier is produced through which runs a series of continuous, zigzag channels. The tower can be completely filled with these tiers, in such a way that they are independent of one another.

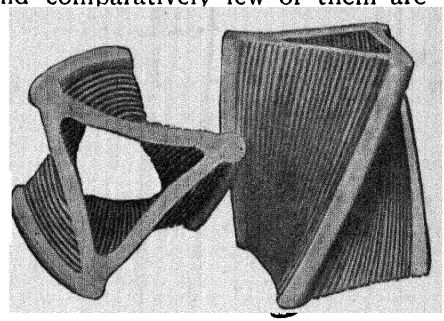


Fig. 117.

P. Kestner (B. P. 170982) forms packing rings from ceramic material by means of cutting punches. They are then compressed and dried.

The Propeller Packing supplied by J. Statham & Sons, Windsor Bridge, Manchester, is illustrated by Fig. 117, which shows the 6 in. × 6 in. element.

They are now making the larger size with the grooving on the inside as well as on the outside, and are hoping shortly to make the smaller size, 4 in. × 4 in., in the same manner.

The following particulars relate to the two sizes:

Size	6″ × 6″	4″ × 4″
Square feet of scrubbing surface per cubic foot	17·5	22·5
Free space when packed	80%	80%
No. per cubic foot	12	36
Weight when packed per cubic foot	34 lb.	29 lb.

Nielsen[1] discusses at length the materials and moulded bodies employed for packing absorbing- and reaction-towers.

[1] *Chem. Trade J.*, 54, 565 and 621.

Camillo Guttmann[1] makes critical remarks upon this. The discussion is continued by Nielsen[2] and Guttmann.[3]

Schobner[4] and Ludwig[5] discuss the various packings for reaction-towers without adducing anything new.

Harris and Thomas (B. P. 7055 of 1915) pack Glover, Gay-Lussac, or like towers with spaced rows of stepped bricks, some of which rest on inward projections of the lining or wall bricks; these projections form grooves for receiving the ends or sides of

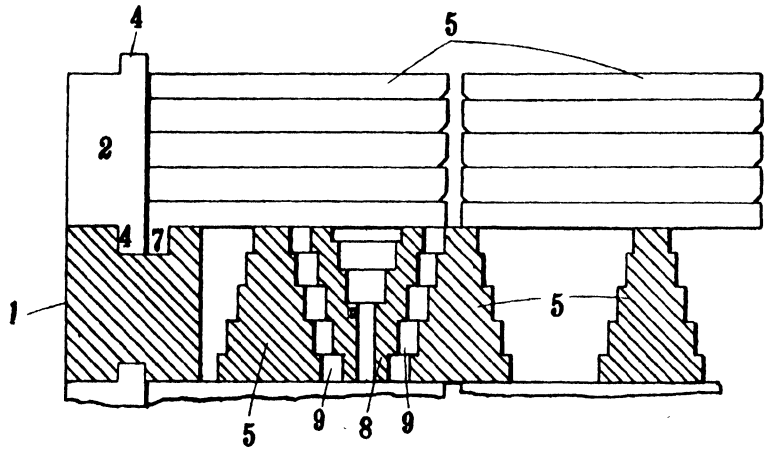


FIG. 118.

the packing-bricks, so that the lining and the packing mutually support each other. The packing-bricks are stepped at the sides only, or also at the ends, and in the latter case have tongues at their upper ends to engage the projections of the lining bricks, these bricks being recessed below the projections, to take the end steps of the packing-bricks. Alternate rows of the packing-bricks may be inverted, and the bricks are then made hollow and provided with distance pieces. For circular tower, the bricks are arc-shaped. Fig. 118 illustrates one form of the packing.

Guttmann (Ger. P. 91815) recommends perforated globular bodies made of earthenware, glass, or metal. As shown in Fig. 119, the perforations are continued into short pipes turning into

[1] *Chem. Trade J.*, p. 671. [2] *Ibid.*, 55, 97. [3] *Ibid.*, p. 98.
[4] *Tonindustrie Zeit.*, 1913, p. 1429.
[5] *Chem. Apparatur*, 1914, p. 271.

the inside of the globe. These bodies may also be undulated inside and outside, to increase the acting surface. They can be put into the tower without any special care in packing. The liquid runs down both inside and outside, and the gases are well mixed.

Niedenführ objects to hollow balls on the system of Guttmann and others, because, firstly, most of the perforations get closed up when filling the tower; secondly, the gases are sure to take the easier way round the balls, instead of forcing their way with increased friction into the interior, and whatever does enter the balls, will remain there for an indefinite time without taking part in the reactions.

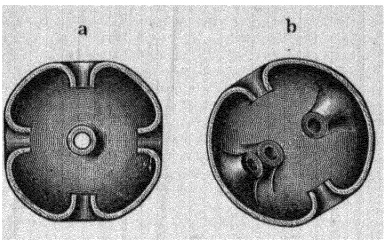


FIG. 119.

Heinz,[1] however, considers Guttmann's globes to be the best possible packing for the Gay-Lussac and for the upper part of the Glover, and also for intermediate towers.

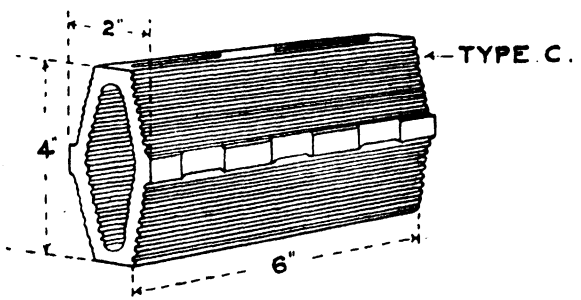


FIG. 120.

The Guttmann Cells (supplied by the Accrington Brick and Tile Co. Ltd.) are illustrated by Figs. 120 and 121. They are claimed to give the following advantages:

1. They cause the gases to change their velocity continuously.
2. They retain a small quantity of liquid, instead of draining away completely.
3. Accumulation of sediment is prevented by having sides at steep angles.

[1] *Z. angew. Chem.*, 1906, p. 705.

4. They give ample free gas space, namely 74 per cent.

5. No skill is needed in packing.

Type B gives 22½ sq. ft. surface per cubic foot, and 11 units are used, weighing 45 lb.

Type C, 34 sq. ft., and 36 units used, weighing 49 lb.

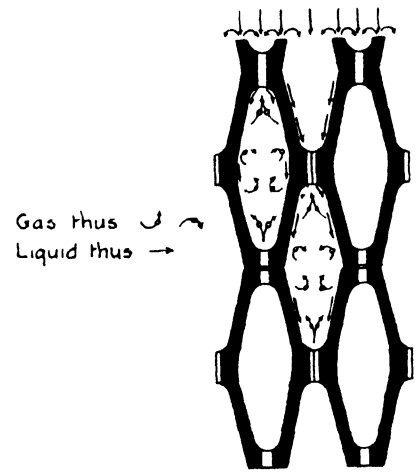


FIG. 121.

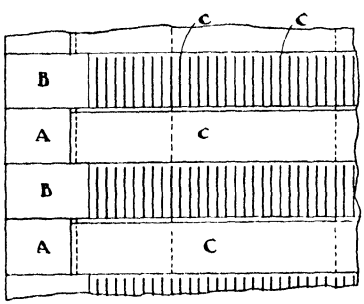


FIG. 122.

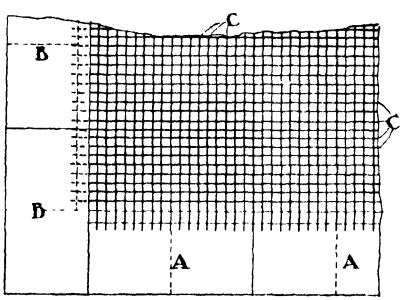


FIG. 123.

W. Wyld and S. W. Shepherd (B. P. 19001 of 1906) pack reaction and Gay-Lussac towers with a series of vertical or inclined glass strips. The ends of these strips fit into grooves of specially shaped bricks, which are built to form a lining of the tower. The depth of the glass strips is slightly less than

that of the bricks, in order to allow a space between the two layers and to avoid the dangers of disarrangement by the structure above resting thereon. The strips may have smooth or roughened surfaces.

Fig. 122 represents the sectional plan of a few courses of scrubbing material using vertical strips, and Fig. 123 is a sectional elevation. Fig. 124 shows a brick with vertical grooves, and Fig. 125 a brick with oblique grooves, which may be inclined all one way, or both right and left as desired.

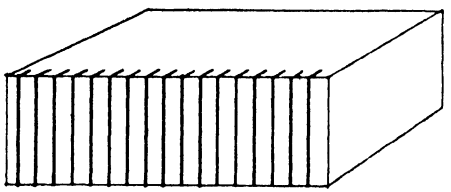


FIG. 124.

Their later patent, No. 8317 of 1907, describes a similar arrangement, but instead of grooved bricks the strips are held apart by distance pieces, which are of suitable size, thickness, and shape to obtain the requisite area for the liquid and vapour space between the strips. By this arrangement there is no need for special bricks; ordinary bricks may be used if placed alternately flat and on edge. (Agent: J. F. Carmichael & Co., Ltd., Tower Building, Liverpool.)

A. M. Fairlie (B. P. 147867 of 1918) describes a filling for towers which is comprised of units having hexagonal or square sides, or otherwise constructed so that they may be fitted against each other without leaving spaces. These units are hollow and have central pillars with helical vanes filling their entire cross-section.

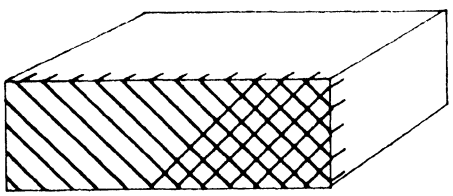


FIG. 125.

R. Lessing (B. P. 139880) describes hollow cylinders in which there is a more or less diametrical partition which may be complete or nearly complete, but is not in such connection with the opposite side that gas and liquid cannot pass it, or is not at all connected with the opposite side. This form is said

to be more efficient than a simple ring, since it offers a larger surface without materially increased obstruction to the passage of fluid.

The packing of Glover towers in England usually consists of flints, picked from the chalk and purified by washing with hydrochloric acid. This material is absolutely acid-resisting and does not fly by the heat, but it does not possess any great surface and is very heavy. For the latter reason, in many places, the upper third of the tower used to be filled with the very hardest coke; but this led to several accidents, by the coke taking fire when there was by chance no feed of acid on. There is also always some action of the acid on the coke, as shown, p. 265 of Vol. I and p. 152 this Vol. Most factories have given it up again, but it may be still in use here and there.

Silica in the form of quartz is frequently employed, but some forms of it are very liable to cracking in course of time, and filling up the gas-channels to such an extent that the draught, and with it the yield, is enormously impaired.

Falding recommends quartz of a vitreous appearance, free from cleavage-lines and admixture with schist or other foreign matter. A little pyrites or oxidised pyrites does no harm, but it must not be present in sufficient quantity to cause a flaw or to cause the quartz to "break down."

The tower rings supplied by many firms are very serviceable for Glover or Gay-Lussac towers, etc. Those measuring 4 in. deep by $5\frac{1}{2}$ in. outside and $3\frac{3}{4}$ in. inside diam. give 15 sq. ft. surface per cubic foot, 48 per cent. free space; fifteen are required per cubic foot and weigh 67 lb. per cubic foot packed. Those 4 in. deep by $4\frac{1}{2}$ in. outside and 3 in. inside diam. give 20 sq. ft. surface, 62 per cent. free space; twenty-four of them being used per cubic foot and weigh 64 lb. (Figs. 128 and 129).

More frequently Glover towers are simply packed with bricks, set on edge, in open work, as in a Siemens's recuperator. These bricks should, of course, resist the action of the acid. Blue Welsh bricks (p. 212) are frequently employed, and even some descriptions of common bricks seem to stand very well.[1] They are, however, always acted upon more or less, and yield

[1] *J. Soc. Chem. Ind.*, 1885, p. 33.

up more iron and alumina to the Glover acid than towers lined and packed with Volvic lava or quartz.

Klencke (B. P. 25027 of 1908) rejects the usual coke or earthenware packing of Glover towers on account of the action of silicon fluoride contained in the burner-gases on such packing. He employs a lead packing, and cools the gases previously by a tower without packing so as to prevent the lead melting.

Even when employing some other kind of packing than bricks (such as flints, cylinders, and the like) it is advisable to place just over the arch two courses of the same kind of bricks

FIG. 126.

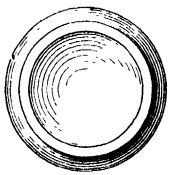
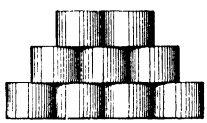


FIG. 127.

FIG. 128.

FIG. 129.



as serve for the lining, pigeonhole-wise, in order to divide the current of gas in a regular way. The packing, of course, must be done systematically and carefully.

Lüty [1] states that the quartz (or flint) packing formerly used in Glover towers has been entirely replaced in Germany, first by acid-proof bricks or slabs, and since about 1880 by cylinders, about 5 in. wide, 6 in. high, and $\frac{3}{4}$ in. thick. With quartz packing, only 12 or 15 per cent. (after some mud has formed, only 10 per cent.) of the tower is empty and free for the reactions; with bricks about 35 per cent., and with cylinders up to 58 per cent. Horizontal surfaces are much less active than perpendicular ones, which are in contact with constantly renewed acid. For this reason, the success of the bricks and slabs is not so great as was expected, no more than that of the Bettenhausen "dividing-cones" ("Verteilungskegel"), as shown in Figs. 126 and 127. But the packing with ordinary cylinders

[1] *Z. angew. Chem.*, 1896, p. 645.

has also led to many disappointments.[1] This is easy to understand if the cylinders are glazed, or if they are placed in such a position that a system of continuous pipes is formed.

The *perforated plates*, on Lunge and Rohrmann's system, described on p. 659 *et seq.*, Lunge, 4th ed., are not very suitable for packing a whole Glover tower; in the lower part the holes would be too quickly stopped up by flue-dust, and

FIG. 130.

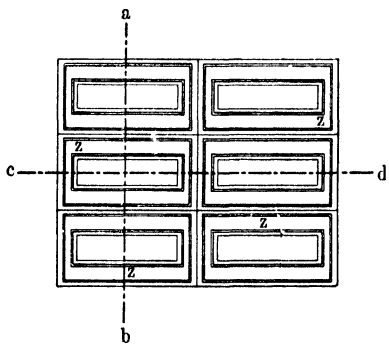
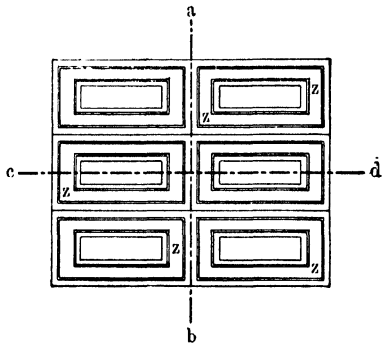


FIG. 131.



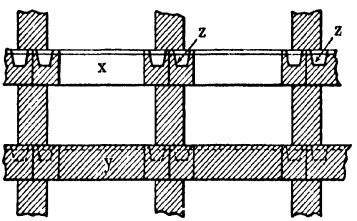


FIG. 132.

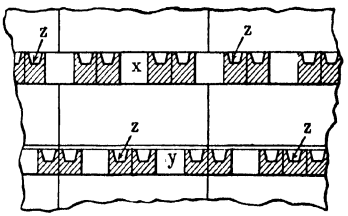


FIG. 133.

the plates would be liable to fracture. They can, however, be employed in the upper half of the tower, the lower half being packed with bricks set edgeways, etc. This plan obviates an objection made to the Nauheim cylinders, viz., that in consequence of their comparatively large size the acid and the gases are not sufficiently brought into contact and the denitration is not perfect.

An excellent application of these plates has been made in a case where it was necessary to bring about the denitration at the lowest possible temperature, in order to avoid losses by the ammonia present in the spent oxide employed. A small tower

[1] Pointed out, *e.g.*, by Guttmann in *J. Soc. Chem. Ind.*, 1903, p. 1331.

of only thirteen layers of plates was put on the top of the ordinary Glover tower. The gases left the latter at 90°, and the plate-tower at 60°. In spite of this slight difference of temperature and of the small height of the plate-tower, it was found to perform 80 per cent. of the denitrating work. Hence the plate-towers must be considered excellently adapted for this class of work, if they can be kept clear of flue-dust (which in the above case was retained by the Glover tower). They must not, however, be flushed out with cold water whilst hot, as this would cause the plates to crack.

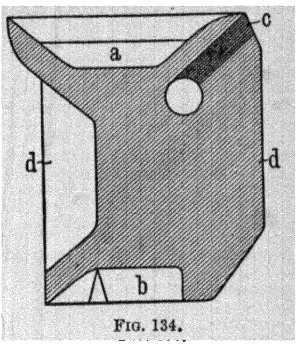


FIG. 134.

A special kind of packing, designed by Niedenführ on the plan of the Lunge-Rohrmann plates, is shown in Figs. 130 to 133. Here the acid is retained on the surface as a shallow layer, and on dropping down is always spread over fresh surfaces, without danger of cracking plates and stopping up holes occurring with the ordinary Lunge plates.

Official information received from the Oker works in 1902 confirms the statement that since 1900 the quartz-packing of the Glover towers has been replaced by "Lunge-Rohrmann" packing of the kind just described and by dishes, with entire success as regards the concentration and denitration of the acid. The acid issues at a temperature of 150° to 160°, the gases at 75° to 80°.

A new shape of stoneware packing for Gay-Lussac and Glover towers (or for distilling columns) is described in the Ger. P. 158715 of Sauerbrey and Wünsche, and shown in Fig. 134. Each of the elements of this packing has a dished head *a*, and a dished bottom *b*, and walls *d d*, with openings *c* connecting these. This special shape is meant to compel both the gases and the liquids to travel in the precise way intended. The liquid runs in a thin stream over the surface, and the gases pass through it without any considerable pressure. These packing elements divide the space of the tower into horizontal layers of small cells, the top and bottom of which have perforations for allowing the gases and the liquid to pass from one layer to the other.

Rabe [1] (Ger. P. 148205) describes, as packing for round or square towers, "angular bodies," as shown in Figs. 135 and 136. They have principally perpendicular planes for the liquids to run down, in a very thin layer, and his calculation

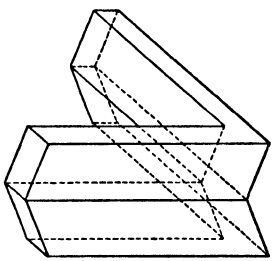


FIG. 135.

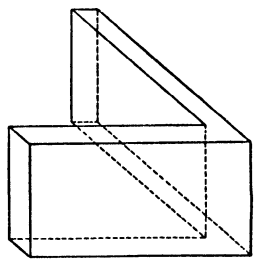


FIG. 136.

makes them ten times more efficient than clinkers of the ordinary shape, and only one-thirteenth as heavy.

Lüttgen (Ger. P. 172445) employs for reaction-towers, etc.,

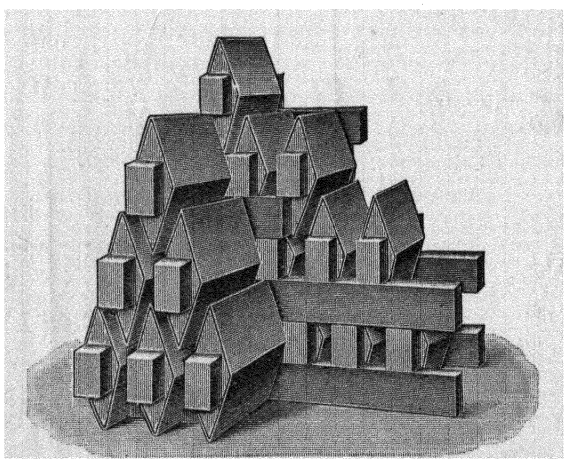


FIG. 137.

a packing consisting of acid-proof stoneware bricks, placed edgeways, of quadrilateral or other section, with lugs in the centre of the ends, and bearers for carrying them on those lugs. Their shape is made clear by Fig. 137.

The Buckley Brick and Tile Company supply tiles of a

[1] *Z. angew. Chem.*, 1904, p. 78; 1906, p. 708.

special design for Glover, Gay-Lussac, intermediate, and other towers, Figs. 138 to 141.

Their efficiency is due to the fact that liquid runs over the "upper side" and clings to the "under side" until it reaches the serrations, where it is broken up to meet the ascending gases, as shown below, and, as the whole surface of each tile is covered with a moving film of liquid, deposits are almost impossible.

The 10-in. × 5-in. × 1½-in. tiles give a free space of 50 per

FIG. 138.

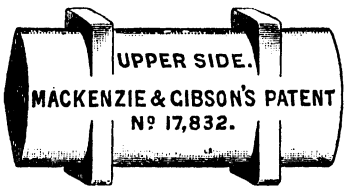
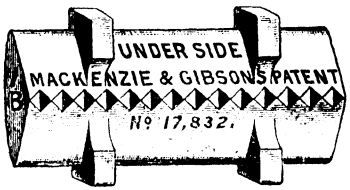


FIG. 139.



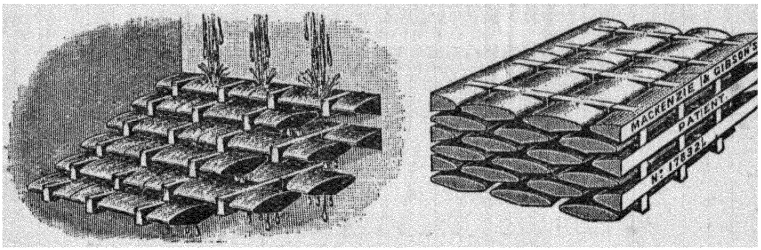


FIG. 140.

FIG. 141.

cent., a surface of 15 sq. ft. per cub. ft. packed, and the 22 units required weigh 72 lb. The 10-in. × 5-in. × 2-in. tiles also give a free space of 50 per cent., a surface of 12 sq. ft., and 17 units are required, weighing 80 lb.

Scherfenberg (B. P. 4366 of 1907; Ger. Ps. 184893 and 239072) describes a packing for reaction and other towers, which is made by the Buckley Brick and Tile Co., Ltd., and sold under the name of "Corrugated Rhomboedric Bricks." They are made in various sizes and require no cross-bearers.

Size.	Sq. ft. surface per cub. ft.	Wt. per cub. ft. packing.	No. of units per cub. ft.
9⅝ × 7 × 3⅝ in.	10·6	61	8
9⅝ × 7 × 2⅜ in.	16·66	61	12
9⅝ × 7 × 1⅝ in.	21·70	61	16

They are illustrated in Fig. 142.

Petersen (Fr. P. 382262 ; Ger. P. 209681) employs perforated V-shaped plates, as shown in Fig. 143.

Green and the Huncoat Plastic Brick and Terra Cotta Co. (B. P. 28004 of 1910) pack the towers with tiles, recessed at the corners to take distance pieces by which they are built into successive floors or layers, each tile being provided with channels and troughs on the upper surface, and a series of ribs and channels on the under surface. Each floor is composed of a series of the blocks laid side by side and end to end, and the floors are arranged so that the main openings through the tiles on one floor are above the blank portions of

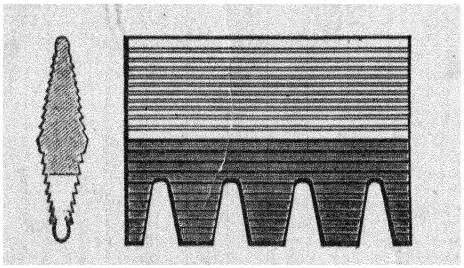


FIG. 142.

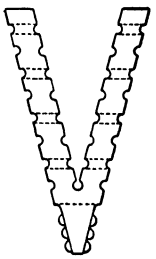


FIG. 143.

the tiles in the next. The ascending gas is broken up and deviated by the channels and ribs on the under surface of the tiles, and while liquid is always lying in the recesses on the upper surfaces, it is being continually changed by the drip of liquid from above and its flow along the channels.

This packing gives a free gas space of 67 per cent., a wetted surface of 7 sq. ft., and the weight per cub. ft. packed is 62 lb. It is stated that the gas travel is two and a half the vertical height of the tower.

The "Obsidianite" packer (B. P. 29126 of 1906) sold by C. Davison & Co., Ltd., is in the form of a rectangular brick measuring 9 in. × 4½ in. × 3 in. over all. The packers with the larger but fewer ribs are used in Glover towers. They are placed in the tower in rows, side by side, so that each rib touches the corresponding rib on the packer next to it on both sides. The packers lie with the hollow up. The superposed rows are put so as to break the joints from side to side, but not from end to end. The packers will then lie in

such a way that two rows of ribs join together, and form a row of square tunnels immediately over the hollow of the packer below them. All the packers must face the same way. In section they will then appear as shown in Figs. 144, 145. When properly placed and set very level the effect is as follows :—

The acid descends from the lutes and fills the topmost

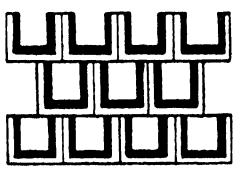


FIG. 144.

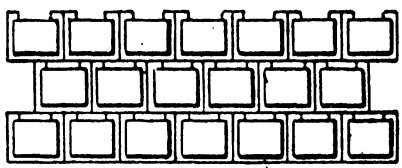


FIG. 145.

reservoirs, which, when full, overflow by the channels formed by the ribs on either side of each packer into the two packers underneath, and so on till this action is multiplied and reduplicated from top to bottom of the tower. They give 14·25 sq. ft. surface per cub. ft., and 21 are used, the weight

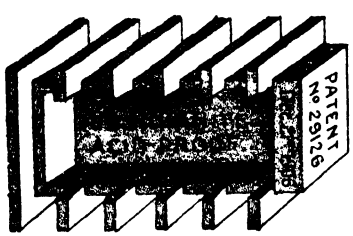


FIG. 146.

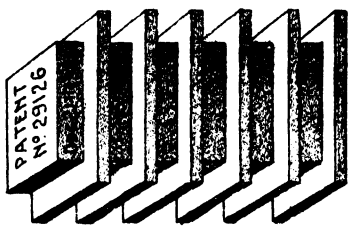


FIG. 147.

being 21 lb. Figs. 146 and 147 show the packer on a larger scale.

Moscicki (B. P. 17355 of 1911) employs a horizontal chamber, properly packed, through which the gases pass in a horizontal direction ; perforated partitions divide it into several compartments.

Fred. C. Zeisberg[1] discusses the various types of tower packings and gives formulæ for obtaining their frictional resistance. He also gives a table showing the characteristics of various packings, from which the following is extracted.

[1] *Chem. and Met. Eng.*, 1920, p. 765.

Similar data for other packings described above have been added.

Type of packing.	Per cent. free space.	Surface sq. ft. per cub. ft.	No. of units per cub. ft.	Weight (lb.) per cub. ft.
Quartz, 6 in.	44	6·3	...	89
,, 2 in.	46	18·7	...	88
Coke, 3 in.	58	12·7	...	29
4 in. × 3 in. smooth diaphragm rings	51	27·0	36	66
1 in. Raschig rings	73	58·0	1350	40
Tiles on edge staggered 1½ in. × 4 in. × 8 in.	75	6·4	9·5	35
Mackenzie & Gibson (Figs. 138-141)	50	(1) 15 (2) 12	(1) 22 (2) 17	72 80
Scherfenbergs (Fig. 142)	...	(1) 10·6 (2) 16·66 (3) 21·70	(1) 8 (2) 12 (3) 16	61
Guttmann cells (Figs. 120, 121)	74	(B) 22·5 (C) 34·0	(B) 11 (C) 36	(B) 45 (C) 49
Davison packers (Figs. 144-147)	...	14·25	21⅓	63·8
Rings 4 in. × 5½ outside diam. (Figs. 126, 127)	48	15	15	67
Huncoat Brick and Terra Cotta	67	7	...	62
Propeller packing (Fig. 117)—				
6 in. × 6 in.	80	17·5	12	34
4 in. × 4 in.	80	22·5	36	29
Wyld & Shepherd's glass strips (Figs. 124, 125)	50	96	192	63

He says that it is important to know the resistance to the gas-flow in any type of packing, and describes the method adopted in obtaining the above data, and continues :—

The free passage of a packing is the interstitial space. It is the space through which the gas must pass and is expressed as a percentage. Thus, a free space of 50 per cent. means that in 100 cub. ft. of packing material 50 cub. ft. of gas passages exist. The free space reported herein was obtained by taking into consideration the number of pieces of packing required to fill a known volume, together with the average weight per piece and the apparent specific gravity of the packing material, or by actually weighing the amount of packing material (the apparent specific gravity of which was known) which was required to fill a known volume. The free space naturally varies with the type of packing and with the manner of disposing it in the tower.

The resistance offered by a tower packing to gas-flow is,

of course, dependent upon both the free space and the surface exposed, but just what effect each might have, it is impossible to predict. For this reason, air was actually blown through a variety of packings under various conditions and the resistance was actually measured.

S. J. Tungay [1] gives an interesting paper upon the principles regarding the use of towers and filling materials.

F. G. Donnan and Irvine Masson [2] give their theory of gas scrubbing material with formula for calculating various data.

The *Alkali Inspectors' Report*, No. 52, for 1915, gives the following particulars relating to the packing of Glover towers in the United Kingdom :—

Description of packing	Bricks.	Flints.	Rings.	Tiles.	Bricks and flints.	Bricks or tiles and rings.	Bricks and tiles.	Total.
Number of towers .	127	130	23	8	28	16	6	338
Per 1000 towers. .	376	385	68	23	83	47	18	1000

[1] *Chem. Age*, 1919, pp. 11-13.
[2] *J. Soc. Chem. Ind.*, 1920, p. 236T.

CHAPTER III

THE CHAMBER-PROCESS

Starting the Chambers.

Covering the Chamber-bottom with Acid.—In order to start a set of chambers, the chamber-bottoms must first of all be covered with acid. This is absolutely necessary when the sides are not burnt to the bottom, but hang loosely down into the upstands, as in that case a hydraulic seal is required to keep the gas within the chamber. Sufficient liquid is present when the sides just dip into it; for, as the lead expands on the chamber getting warm, and as the liquid constantly increases by condensation, the hydraulic seal is constantly improving. However, for reasons to be stated hereafter, it is preferable to make the depth of acid as great as possible from the outset. Only in extreme cases should *water or very weak acid* be taken for luting the chamber. If it can be done, the proper thing is to bring the bottom-acid at once to at least about 90° Tw., or better, to 100°. If this cannot be effected, this strength ought to be approached as nearly as possible. The objection to starting a chamber with water or very weak acid is, that the vapour of nitric acid dissolves in the bottom-liquid and acts upon the lead.

Even if all the nitric acid freshly supplied were decomposed by sulphur dioxide before reaching the bottom, the presence of water or very dilute acid in large quantity would cause the new formation of large quantities of nitric acid from the lower oxides of nitrogen (N_2O_4, N_2O_3, and NO), and, on the other hand, of nitrous oxide, N_2O. There would thus be a great loss of nitre in both forms, apart from the action of the lead, and the reactions within the chamber would be quite irregular.

The chamber-process only goes on properly when there is an abundant quantity of fairly strong acid at the bottom of the chambers. If the sides are burnt to the bottom, it is preferable even to start a chamber dry rather than start it with water; but otherwise a layer of about 4 in. of acid on the bottom of the chambers is preferred.

When the chambers are luted with acid, and the burners are heated up so that they can be charged, the connection between them and the chambers is made and the burner-gas allowed to enter. Of course, sufficient draught is given and nitric acid is admitted at once. At first little or no steam is allowed to enter, as it would dilute the bottom-acid too much. The nitric acid is introduced either as vapour or in the liquid form. At first, about three or four times the amount required for normal running is put in, because there must be a stock of nitre-gas in the chambers. Subsequently this stock need be renewed only in so far as any loss is suffered. At the beginning, from 12 to 15 parts of nitrate of soda, or a corresponding quantity of nitric acid, must be employed for 100 parts of sulphur, and this addition must be continued till the gas in the last chamber turns yellow. The quantity is then gradually diminished till the correct point is reached.

MacCulloch[1] suggests starting the chambers by admitting steam and nitre-gas from a steam-column for five or six hours before the burner-gas is admitted. In that case, he says, the chambers work well from the first, and in one instance showed acid of 1·65 at the drips in twelve hours. This may be so; but the process, while saving a little time and possibly a little nitre, from the outset detracts much from the durability of the chambers, since during the five or six hours when they receive only steam and nitre-gas very much nitric acid must condense, and whatever is gained by the drips is again lost by the previous dilution of the bottom-acid.

As soon as the drips and test-plugs prove that sulphuric acid is already forming in the chamber, *steam* is admitted (or increased), but at first with great caution. Then all the factors of acid-making are at work, and the same rules are now valid as for the ordinary working of the process. If

[1] *Chem. News*, 27, 136.

everything is in proper order, and if plenty of nitre (which is mostly recovered in the Gay-Lussac tower) is used, a chamber may be in regular working order on the fourth, sometimes even on the third day after starting.

The opposite case must also be taken into account, viz. *when a set of chambers has to be stopped for repairs.* It may be necessary to do so for one or two days, and it is, of course, most important to be able to go on again as quickly as possible, without losing too much nitre. If the proper precautions are neglected, it is possible that so much nitric acid is produced that the chamber-lead is seriously acted upon. To avoid this, it is best to proceed as follows:—First of all, the pyrites-burners are stopped; no fresh charge is put in, and all openings are closed as tightly as possible. After this the supply of nitre is stopped, but the supply of steam is continued, as long as the gas of the last chamber shows any outward pressure. When this has gone and there is some inward suction, the outlet damper is closed, and air is allowed to enter at some lute, manhole, sight, etc., to avoid the forcing-in of the chamber-walls by the atmospheric pressure. At this stage a good deal of acid is produced, as is proved by the action of the drips; but the steam should be shut off as soon as the drips go down to 100° Tw. When the drips cease to act all openings are shut. If the burners are started again within three days from the stoppage, it is only necessary to put on a good supply of nitre to get the chambers to work again. The regulation of the steam must, however, be as carefully attended to as when starting a new set of chambers.

Supply of Air.

The object of a regular chamber-process is of course this—to make from a given quantity of brimstone or pyrites the greatest possible quantity of sulphuric acid with the smallest possible consumption of nitre. It must also be mentioned, as less decisive, but still of importance, that the chamber-acid should be as strong as is compatible with the two conditions just stated and also with the prevention of damage to the chamber-lead. In order to attain that object, the attention of the chamber-manager must be directed to many points,

some of which have already been treated of in detail, whilst others will be enlarged upon here.

1st. *Complete Combustion of the Sulphur-ore.*—This, with brimstone, follows as a matter of course; with pyrites it is much more difficult (p. 328 *et seq.* of Vol. I).

2nd. *Proper Composition of the Burner-gas.*—This has been dealt with in the fourth chapter of Vol. I, and it is sufficient here to repeat, that the proper composition of the burner-gas depends almost entirely upon the regular supply of air produced by proper regulation of the draught. It has already been shown (p. 349 of Vol. I) that, apart from chemical analysis, there are practical tests to show at the burners whether the draught is right or not. At the chambers also this must equally be attended to by means of the lutes or the test-plugs (p. 103), by pressure-gauges, or by anemometers (pp. 103 and 106). Generally, the following rules may be laid down as a rough guide :—

In a set of three chambers the first chamber should show an outward pressure, and, accordingly, the gas should issue whenever a plug is removed. In the middle chamber the gas should be almost in equilibrium with the outer air, but there should be rather a little outward pressure than suction. In the last chamber there may be some, but very little, suction, and behind it, but before the damper, the suction should be very perceptible.

Generally, it may be said that the draught must be sufficient to cause a proper working of the burners with resulting proper composition of the gas, but *no more than this.* The draught should be observed not merely by practical indications, but by testing the burner-gas for SO_2 and the exit-gas for O. The rule given can be stated more precisely in this form :— So much draught should be given that the burner-gas from brimstone approaches 11 per cent. SO_2, that from pyrites 8 per cent. as far as circumstances permit, and that the gas issuing at the end still contains 5 or 6 per cent. of oxygen (*cf. infra*).

A most important control of the working of the chambers, so far as the draught is concerned, is exercised by *testing the exit-gases for oxygen*, as has been described (p. 479 of Vol. I), and as will be mentioned later on in this chapter. There is no agreement on the question as to what is *the proper*

percentage of oxygen in chamber exit-gases. There is, however, general agreement that a certain excess of oxygen is required, over and above the theoretical quantity, in order to promote and hasten the regeneration of nitric oxide to nitrous acid, etc. Bode[1] assumes as a minimum 6 per cent. of free oxygen in the exit-gas of the chambers, and mentions that at 8 per cent. free oxygen the yield had been quite as good as, and the consumption of nitre even a shade better than, at 6 per cent. According to Hasenclever[2] in 1866, before Schwarzenberg, Gerstenhöfer had already calculated the theoretically best composition of burner-gas, but had only communicated it privately to several factories. His figures, which do not materially differ from those quoted (pp. 458 and 460 of Vol. I), are: for brimstone,

10·65 per cent. by volume of SO_2,
10·35 „ „ „ O,
79·00 „ „ „ N;

for burning pyrites,

8·80 per cent. by volume of SO_2,
9·60 „ „ „ O,
81·60 „ „ „ N.

Scheurer-Kestner also assumes that the percentage of oxygen in the exit-gas is 6 per cent. He has, however, proved that the oxygen in the *burner-gas* is considerably less than is shown in the above calculation, probably owing to the formation of SO_3 (p. 463 of Vol. I).

If it is established that a certain excess of oxygen increases the energy of the action in the chambers although its presence increases the volume of gas, it is, on the other hand, at least as well established that too great an excess of air diminishes the yield and seriously increases the consumption of nitre. Lunge in his 4th edition, p. 909, recommends working with 5 or 6 per cent. of oxygen at the exit. The writer, however, always worked with rather higher figures, and in the case of spent oxide or coal-brasses, he found the most economical working was with 9 per cent.

Of course, the tests taken at the exit are often unduly high,

[1] *Beiträge*, p. 15.
[2] *Hofmann's Report*, 1, 370.

due to air entering the process from leaky chambers and connections, and he prefers taking the test at the burner-pipe entering the Glover tower.

Excessive draught acts in different ways, according to whether the admission of air to the burners is regulated in the proper manner or not. If the action of the excess of draught extends to the burners, they will become too hot; sulphur will be sublimed, especially from brimstone-burners, but even from pyrites-burners, and in the case of lump burners scars will be formed. If, however, the excess of draught is *very* great, the burners may, on the contrary, become cooled by the excess of air.

If the admission of air below the burner-grates is regulated so that these do not receive too much air, an excessive draught at the end of the system must produce a diminution of pressure in the chambers; air is then aspirated through the tiniest chinks and crevices, and in very bad cases, the sides of the chamber may be drawn in.

In both cases "false air" (which means too much oxygen and inert gas) gets into the chamber, the chamber-space is badly utilised, and the excess of gas carries away sulphur dioxide and nitrous gases. If the attempt is made to prevent this by employing more nitre, too much work is put upon the Gay-Lussac tower and more nitre will be lost than in a regular way.

In the case of *insufficient draught* at the end of the system, there will be too much pressure in the chambers, as the hot gases continue to come over from the burners; after a short time there will be a deficiency of air in these, which will be shown by the analysis of the burner-gas and end-gas; the burners will become too hot, as the cooling effect of the air will be missing. Generally this is accompanied by gas blowing out from the burners. This might, of course, also be caused by any kind of stoppage in the gas-flue, but in that case the pressure in the chambers is not too great, but the reverse. All this again leads to an excessive consumption of nitre, as the lower oxides of nitrogen do not meet with sufficient oxygen, and even NO may be lost as such.

Either condition leads to a bad yield of sulphuric acid, large consumption of nitre and escape of sulphurous acid into

the air. Further proof is not required to show the importance of regulating the draught as accurately as possible.

The regulation of the draught takes place principally, or sometimes even exclusively, at the exit end by means of the contrivances already described (p. 124 *et seq.*). It is not practicable to depend for regulation entirely on the air-inlet holes of the burners, as these must be adjusted to suit each individual burner. It is very important that the gas-pipes between the burners and the Glover tower and the chamber should be examined, as they may be partially stopped up with deposit. In this case, the draught at the burner will be bad and will be but slightly improved by opening the exit-damper. This cannot be overlooked if the process is properly controlled by regularly testing the burner-gas and exit-gas; if the latter shows enough or more than enough free oxygen while the burner-gas is blowing out, there must be some intermediate stoppage. The lutes or side-plugs fixed in various parts of the set will materially assist in localising the stoppage.

Some acid makers prefer working in such a way that there is always ample draught from the burners into the first chamber. They employ large and very loosely-packed Glover towers. The burners in this case never blow out, and yet the chambers themselves can be worked right to the end with even outward pressure instead of inward draught. There must then be, however, the drawback that, owing to the loose packing, the denitration in the Glover tower will not be perfect.

Some chamber-managers contend that no further regulation of the draught need take place at the outlet when this has once been done, as the outside atmospheric conditions never vary sufficiently to interfere with the working of the process. This opinion is decidedly wrong. In most parts of Central Europe the temperature may vary by 40°, or even more, between the extreme heat of summer and the extreme cold of winter. This means that for every 1000 cub. ft. of air required in the coldest season, nearly 1150 cub. ft. must pass through the apparatus in the hottest season, supposing the barometric pressures to be equal; but these latter may vary 30 mm., or even more, and 1000 cub. ft. at 760 mm. pressure, for instance, represents the same weight of air as 1041 cub. ft. at 730 mm.

Combining both (and very frequently low temperatures and high barometric pressure go together, as well as high temperatures and a low barometer), 1000 cub. ft. in winter may be equal in weight to 1200 cub. ft. in summer. It is quite evident that such large differences, and even much smaller ones, as may occur from day to day, *must* be compensated by regulating the outlet of the gases accordingly. Nor must it be overlooked that the pressure of wind affects the quantity of gases passing through a given orifice, and this circumstance sometimes has a very serious effect on the draught, even when the burner-house is sheltered, as it ought to be, against the direct action of gusts on the ash-pits, or furnace doors. N. L. Heinz (U.S. P. 1057149) suggests mixing the steam, the nitrous and the sulphurous gases, with regulated quantities of air in various places in such a way that the gas current in the chambers keeps at constant pressure, the quantity of oxygen contained in the air introduced being equal to that consumed by the reaction of the gases.

Supply of Water (Steam).

The regulation of the steam or water-spray is one of the most important parts of chamber-management, and should always be taken in hand by the responsible foreman or superintendent himself. One of the first conditions necessary is that the tension of the steam should be kept as constant as possible. It is hardly necessary to point out how much this task is facilitated by registering steam-gauge or by automatically regulating steam-valves (p. 106). The round of the chambers should be made two or three times a day; at some works it is even made every other hour. It is one of the advantages of the water-spray system (p. 109 *et seq.*) that there are hardly any variations in the quantity of water supplied, but other difficulties may occur instead (p. 263).

It must be borne in mind that the Glover tower supplies the first or "leading" chamber of a set with a good deal of the steam required. Hence steam or water-spray must be supplied to this chamber in much smaller quantity than when working without a Glover tower, and the position of the jets is also influenced by this (*cf.* p. 108).

A rough indication of whether too little or too much steam is present, is sometimes sought in the appearance of the glass jars covering the lutes of the chambers (p. 103). If these show a white crystalline covering of chamber-crystals, which are proved to be such by their turning green on being moistened, there is evidently a deficiency of steam. If, on the other hand, the glass jars are dripping wet, there is too much steam in the chamber. This is, of course, only to be taken in conjunction with the other observations to be made by the attendant.

The proper indicator for the admission of steam or water is the *strength of acid made in the chamber*, both as observed in the acid-drips (p. 102) and in the bottom-acid. These two are never identical. The drip-acid is, other than in exceptional cases, stronger than the bottom-acid (see below). In long chambers there is a considerable difference between the front and the back part, and these chambers should be provided with at least two sets of drips.

Considerable difference of opinion exists as to the *strength of acid* most conducive to a proper working of the vitriol-chambers—that is, to the best yield, the greatest production for a given chamber-space, and the smallest consumption of nitre. The chamber-acid is generally kept much stronger in the majority of English works than in the majority of Continental works. Whilst the former mostly keep the acid in the leading-chamber from 120° to 130°, and the drips often 5° to 10° higher, the usual practice on the Continent is to keep the acid at 106° to 110°, or at most 116° Tw. From the writer's experience with a set of four chambers working on 44 per cent. pyrites, the following strength of drips was aimed at: No. 1 Chamber, 110° to 120°; No. 2, 105° to 115°; No. 3, 95° to 105°; and No. 4, 90° to 100° Tw. The chamber-space was 10 to 12 cub. ft. per lb. S. per 24 hours and the nitre consumption, taken over a period of several years, was under 0·9 per cent. on the O.V. made.

It is unnecessary to say that both English and Continental manufacturers firmly believe that they are in the right, the former in making stronger, the latter in making weaker chamber-acid. Both contend that in their, and *only* in their way, the best results are obtained. It is difficult, if not impossible, to arrive at any certain decision on the question

from a comparison of the data supplied by various works as to the strength of acid, the yields, the consumption of nitre, the chamber-spaces, and so forth. This difficulty arises both from the complication of the various conditions, which react upon one another, and from the very frequent inaccuracy and incompleteness of the figures obtainable.

All *theories* of the vitriol-chamber process seem to point to the preference of the *weaker* rather than of the stronger acid. Hurter, in his dynamical theory,[1] arrives at the result that the chamber-space required is inversely proportional to the quantity of nitrogen compounds present, and to the amount of water present in the gaseous condition; in other words, that, other conditions being equal, the quantity of acid produced within a given chamber-space is larger when weaker acid is made than when strong acid is made. It is true that the evidence given for this from the actual results of a number of chambers is very scanty, and certainly not sufficiently conclusive in itself. This was unavoidable, as only works which did not possess Gay-Lussac and Glover towers were quoted. But, at all events, no contrary assertion can be based on that evidence.

The theory propounded by Lunge, and the very similar one by Sorel, both of which will be found at the close of this chapter, also demand that, other conditions being equal, the sulphuric-acid-forming reaction is promoted by a larger amount of water, up to the limit where an excess of water would produce other injurious reactions.

Another point to be considered is this, that it is practically impossible to prevent the loss of some nitre, dissolved in the chamber-acid as nitrosulphuric acid, but that the tendency of the chamber-acid to retain nitre in this form rapidly increases with its strength. Theory would therefore demand keeping the acid weaker in order to lose less nitre. Whether this is so or not in practice can only be proved by bringing together a great amount of *reliable* data; the difficulty of doing this has been pointed out before. It is a fact that sometimes "pale" chambers are the consequence of giving too little steam (that is, keeping the acid too concentrated), and this evil can be remedied by turning on full steam for a short time, which causes the chamber to become red again.

[1] *J. Soc. Chem. Ind.*, 1882, p. 10.

The usual, and practically the only reasonable, motive of English manufacturers for making their chamber-acid so much stronger is, of course, that they save the expense and trouble of concentrating the acid for use or sale. But there is little or nothing in this in the great majority of cases. For the manufacture of superphosphates, which requires an enormous quantity of sulphuric acid, and for which many acid-works are exclusively employed, the strength of 110° Tw. is quite sufficient. For decomposing salt, and for making rectified oil of vitriol, a higher strength is certainly advantageous. But at every works provided with Glover towers (that is, at every properly equipped works, and actually in the great majority of existing factories) there is no difficulty whatever in bringing all the acid up to 148° Tw. without any expense, even when starting from chamber-acid at 110° Tw.; and this is done even without Glover towers at many works by means of the waste heat of the pyrites-kilns.

It is difficult to say anything general as to the strength at which the *drips of the first chamber* ought to be kept. At one works the drip acid is found to be only 2° or 3°, at others 15° or more above the bottom-acid. At others it is always weaker than the bottom-acid. Everything depends on the position of the drips. It is certain, however, that in the same plant the difference between the strength of the drip-acid and that of the bottom-acid is nearly constant, and that the attendant must manage his chambers accordingly. On the average, the drips, where they are taken from the inside, away from the chamber-sides, show about 10° Tw. more than the bottom-acid; but this only holds good for the ordinary style of working.

It has been seen (p. 213, Vol. I) that the tension of aqueous vapour varies both with the temperature and with the strength of the acid; for instance, at 80° (near the chamber-side), acid of 114° Tw. has exactly the same vapour-tension as acid of 128½° Tw. at 95° (only 2½ in. within the chamber). Sorel observed that the acids collected at various points of the same transverse section of the chamber really showed these differences of strength, and that, therefore, it may be said that they are all in equilibrium with aqueous-vapour of the same tension. This shows how useless it is to compare the drips of different

sets of chambers, unless they are fixed in a precisely similar position to one another.

Under normal conditions *the strength of acid in the second and following chambers* is always below that of the first chamber. The second chamber, in a set of three, has generally about 10° Tw. less than the first. In a set of four or more chambers the strengths will naturally diminish gradually.

In the presence of a Gay-Lussac tower there is no reason whatever for keeping the last chamber below 90° Tw., or even a few degrees above this. No formation of nitric acid is to be apprehended, and the gases will be better dried in preparation for the Gay-Lussac tower. The practice of some works to go down as low as 75° or 80° Tw. in the back chamber cannot be recommended.

Crowder[1] prefers placing the "drips" in the connecting-pipes between the chambers, and keeps them as nearly as possible at the following strengths:—Drip from Glover tower to 1st chamber = 95° to 105°; from 1st to 2nd chamber = 130°; from 2nd to 3rd chamber = 122°; from 3rd to 4th chamber = 105°; from 4th to Gay-Lussac = 85°. If the drip from No. 1 to No. 2 chamber stands lower than 130°, the consumption of nitre is increased. [The drips in the connecting-pipes do not correctly indicate the work done in the chamber, as, in consequence of the far greater cooling-action, the formation of acid in these places must be abnormally large.]

The injurious results of a wrong supply of water (as steam or spray) to the chambers are as follows:—

The first and most obvious result of giving *too much steam* is, that the acid gets too weak. But this is of less importance than another drawback which follows from the same cause. If the lower oxides of nitrogen meet with an excess of oxygen (which is always present in the chambers) *and at the same time with an excess of water*, the following reactions take place:—

$$2NO + 3O + H_2O = 2HNO_3;$$
$$N_2O_3 + 2O + H_2O = 2HNO_3.$$

That is to say, they are converted into nitric acid, which, in the first instance, is a much less efficient carrier of oxygen than

[1] *J. Soc. Chem. Ind.*, 1891, p. 301.

nitrous acid, and, secondly, is to a great extent dissolved in the bottom-acid ; here it assists the acid-forming process very little, and, moreover, acts upon the lead. So long as the bottom-acid is fairly strong (say, up to 90°), it will not retain the nitric acid long, but will again give it off as lower nitrogen oxides on account of the action of sulphur dioxide. If, however, the excessive supply of steam continues, it will soon keep the nitric acid back, and as the process is thereby disturbed, even the steam[1] which should have been used up in the formation of sulphuric acid is condensed to water, and the dilution of the bottom-acid is thus again increased. If this state of matters has once set in, it is not always easily remedied. Cutting off the steam is not sufficient ; much more nitre must be put in as well, and even then the bottom-acid only gradually gets up to its normal strength. In the meantime the yield falls off, the consumption of nitre increases very much, and the action of the nitric acid on the chamber-lead does permanent damage. Thus it is apparent that an excess of steam does very much harm, and great care must be taken lest the strength of the acid should go down below the proper concentration. The chambers soon show when they have too much steam by becoming pale. A pale chamber often gets red again an hour after the supply of steam has been partially cut off.

An excess of steam has another injurious effect, which can only be explained in detail when dealing with the theory of the chamber-process, viz., the formation of nitrous oxide, or even of elementary nitrogen, whereas normally the reduction of the nitrogen-acids ought not to go beyond nitric oxide. Neither nitrous oxide nor nitrogen can be reoxidised to nitrogen-acids ; they escape with the other gases, and thus cause a loss of nitre.

It is advisable, also, to consider the opposite case, viz., that *the chambers receive too little steam.* According to the theory of the vitriol-chamber process, to be developed later on, this must alter the conditions for the formation of sulphuric acid, since the substance formed as an intermediate state, viz. nitroso-sulphuric acid, cannot then be entirely decomposed into

[1] Whenever "steam" is spoken of in connection with the supply of moisture to the chambers, water in the form of spray or mist is also included.

sulphuric acid and nitrous acid. It will in this case be either separated in the solid state, as "chamber-crystals," or else it will dissolve in the bottom-acid. In actual practice it rarely happens that the deficiency of water is so great as to lead to the formation of solid chamber-crystals within the chambers; more frequently this happens in the connecting-pipes. But it is unavoidable that some chamber-crystals (commonly called "nitre" in this case) dissolve in the bottom-acid. It will be seen later on that a certain quantity of "nitre" *must* be present in properly working chambers; but if there is too little steam, this quantity will be largely increased, both by a deficiency of water in the acid mist floating about, which leaves a large quantity of nitrososulphuric acid undecomposed, and by the excessive concentration of the bottom-acid, which enables it to hold more "nitre" in solution. Thus the nitre will be removed from its proper sphere of action, viz., the atmosphere of the chamber, and SO_2 will escape oxidation. Where the chamber-acid is used directly, without first passing it through the Glover tower, this nitre will finally be lost. All this, of course, happens less easily where the bottom-acid is kept at a lower strength; there is in this case more time for repairing a temporary deficiency of steam, as indicated by testing the drips and bottom-acids for strength and nitre.

A deficiency of steam has also the following effect, that the acid by becoming too concentrated may to some extent act upon the lead. So long as the strength of the chamber-acid does not exceed 144° Tw. (and this will very rarely happen, even with faulty management), there is not much harm done. For very good reasons, the last chamber, if a Gay-Lussac tower is present, receives very little steam; in the case of smaller chambers (tambours) none at all. This, however, may be carried too far. Then, in spite of the dark-red appearance of the chambers, there is a bad yield of acid, because the water necessary for its formation is missing, and SO_2 and O pass away uncombined. This occurs especially when the chamber shows a very clear, transparent red, instead of being somewhat dim and misty.

On the whole, it is evident that the risks run by a deficiency of steam are not nearly as serious as those arising from an excess of steam.

Hurter[1] gives the following rules for utilising the indication of the chamber-drips :—

1st. If the strength of the acid in the drips is *correct* but the quantity is deficient, the chamber is short of nitre.

2nd. If the strength is *high* and the quantity not far short, the chamber is very rich in nitre ; but if the quantity is short, it has too little steam.

3rd. If the strength is *low*, but the quantity great, the chamber has too much steam. If, on the other hand, the strength is low and the quantity short, the chamber is very poor in nitre.

It is needless to say that the indications afforded by these rules would be sometimes very misleading, the conditions being too complicated, if they were not supplemented by direct observations of the amount of "nitre," the temperature, and the composition of the inlet- and outlet-gases, as shown below.

Stinville (Ger. P. 144084) produces in the lead-chambers a circulation of cooled acid, diluted to such an extent that its steam tension is sufficient to furnish the aqueous vapour required for the process. There are three chambers, *a*, *b*, *c*. The gases pass from the Glover tower into *a*, and leave *c* for the Gay-Lussac tower. The bottom-acid flows from *c* to *b*, from *b* to *a*, and from *a* into a cooler, where it is cooled down by means of a water-coil and also diluted by fresh water ; in this state it is pumped back again into the chamber *c*.

Supply of Nitre.

It is quite evident that those ingredients from which sulphuric acid is ultimately formed, viz., sulphur dioxide, atmospheric oxygen, and water, must be supplied to the chambers in proportions varying within very narrow limits, as any undue excess or deficiency of one of these will cause a corresponding waste. Sulphur dioxide being taken as the fixed quantity, the proportion of water supplied is kept so that an almost constant concentration of chamber-acid is obtained, and the supply of air is regulated by the draught in such a way that a certain necessary excess of oxygen, but no more than this,

[1] *The Manufacture of Sulphuric Acid*, Liverpool, 1882, p. 16.

is found in the exit-gas. But the matter is different with that reagent which does not enter into the composition of the ultimate product, and serves only as an intermediary agent for combining SO_2, O, and H_2O, without (in theory) suffering any real change or loss at the end of the process. This type of agent is now called a catalyser (see later on), and in this case is, of course, the "nitre," under which expression are included all the compounds of nitrogen which are concerned in the manufacture of sulphuric acid, at whatever stage of oxidation or combination they may exist at any moment.

It is almost self-evident that the acid-making process can be made more or less rapid by supplying more or less nitre, and that this finds expression in the greater or smaller space which the process requires. In fact, considerable variations may be made in the supply of nitre, according to whether the chamber-space is to be utilised as fully as possible or not; and up to a certain extent it may be said that the supply of nitre must change in an inverse proportion to the chamber-space present. But certain limits do exist here as well. If there is too small a supply of nitre, the reactions become too sluggish and very disastrous consequences follow, which cannot be avoided by any amount of chamber-space; and if too much nitre is supplied, the temperature rises too much, the chamber-lead is acted upon, and part of the nitre escapes recovery. This subject will be referred to in detail later.

The *supply of nitre* must be regulated on entirely different principles, according to whether there is an apparatus for the recovery of nitre or not. In the latter case, care must be taken that there is not too much nitre-gas in the last chamber, since everything issuing from it is a total loss. Therefore the gas in the last chamber but one is kept strongly yellow or red, in order to promote the acid-forming process, but in the last chamber the colour is only faintly yellow.

The bottom-acid in that chamber, which is usually kept at 50° Tw., or even below, will partly absorb the nitre-gas as nitric acid, and there will not be so much of it lost. This is attained in the last chamber by giving it more steam. It will be seen at once that in this chamber very little work can be done without a very great loss of nitre; for the oxidation of

sulphurous acid goes on all through the chamber only if the nitre be present in large quantity. Therefore one of two things must be done: either a large quantity of nitre must be sacrificed in order to utilise the last chamber, or the last chamber is practically used for recovering part of the nitre, in which case a third or fourth of the chamber-space is sacrificed, with a corresponding decrease in the amount of sulphur burnt in that set. The last chamber is not merely a costly, but also a very inefficient apparatus for recovering the nitre, as the nitre used must be increased to 10 per cent. of the weight of the sulphur if a good yield is to be obtained. With poor, badly burning ores, of course, even more nitre is consumed, corresponding to the excess of air.

These considerations will make it evident how much more rational it is to *recover the nitre* by a proper apparatus. We thus effect a saving of a fourth, up to a third, in chamber-space, at least one-third in nitre, and also have a better yield, because, up to the last, an excess of nitrous gas is present, and no sulphurous acid can escape oxidation. In this way, the escape of noxious vapours is also more completely prevented. The construction of the nitre-recovery apparatus, and everything pertaining to it, has been described in Chapter II. Only the method of managing the chambers will be described here. Supposing the set to consist of three chambers, the first chamber, into which in all cases both the gas from fresh nitric acid and that from the nitrous vitriol are introduced, whether it be by nitre-ovens, ammonia oxidation units, Glover towers, or steam-columns, will always have an excess of nitre-gas. In spite of this, the characteristic colour of nitrogen peroxide will not be perceived in the first chamber, both because the sulphur dioxide, likewise present in excess, constantly reduces most of the NO_2 to colourless nitric oxide, and because the formation of sulphuric acid, principally going on in this chamber, generates in large quantities the well-known heavy white clouds. The whole atmosphere of the chamber is filled with these, and, owing to its opacity, its colour cannot be clearly recognised. In the second chamber the atmosphere is much clearer, and as there is also very much less sulphur dioxide present, a portion of the higher nitrogen oxides will be perceived by their peculiar colour. There is, however, still so much sulphur dioxide present,

that the mixture of gases in the second chamber will only show a more or less reddish-yellow.

In the third chamber, however (in a set of more than three chambers, the last—in a single chamber, in its last portion), the nitre-gas should largely predominate. There should be very little sulphur dioxide remaining here, and before the gas issues out of the chamber into the Gay-Lussac tower most of the sulphur dioxide ought to be removed from it. This is only possible by a large excess of nitrogen acids; and as, according to previous explanations, there is also oxygen present (5 to 6 per cent. by volume), that excess will consist not only of colourless nitric oxide, but also of red nitrogen peroxide. This is proved by the last chamber showing a dark red colour, sometimes so deep as to be opaque. Even in the much shallower layer of gas observed in the "sight" of the pipe leading to the absorbing-tower, the red or orange colour should be quite decided. Within the chamber the red should not be quite transparent, but dimmed by a mist of water.

The *colour of a chamber* can be observed by opening the lutes or the plugs, but in a much more convenient way by glass windows put in the sides of the chamber itself (as described, p. 103). If the last chamber turns paler, the cause of this must be sought. It may be that it has got too much or too little steam or too little nitre; but it is always a sign that something is wrong. By comparing the other symptoms, especially the strength and the nitrogen content of the drips and bottom-acids, the special cause of the fault must be ascertained. When the last chamber becomes quite pale, it is certain that a great loss is suffered by sulphur dioxide escaping from it, and this gas on its way through the Gay-Lussac tower will even denitrate the nitrous vitriol contained therein, and cause a loss of nitre in the shape of nitric oxide escaping into the outer air. Everything must therefore be done to avert the last chamber turning pale.

Apart from the colour, the gradual diminution of sulphur dioxide and the increase of nitrogen acids in the chamber-gas as it proceeds on its way can be perceived from other signs, such as the *smell* and the *chemical analysis* of the gas. The judgment by smell is so much more uncertain and inexact than by colour that it is not worth while to study it in detail. A

chemical analysis of the gas would certainly permit the reaction in the individual chambers to be traced with ease and safety; but this plan is not usual, and even the best works regularly make only two gas-analyses—that of the burner-gas before entering the chambers, and that of the gas finally leaving the apparatus as it issues from the Gay-Lussac tower. It would give some little trouble to analyse the chamber-gas, and this is not necessary, since its colour gives a sufficient indication for the purpose in question. It is now considered of much more importance that the temperatures of each chamber should be noted, for this has a very marked effect in the satisfactory working of the process (*vide infra*).

In addition to testing the *chamber-acid* for its strength, it is of great importance to test it also for its nitrogen content (percentage of nitrogen acids). This forms a necessary complement to the observation of the colour of the chambers. Under normal circumstances the percentages of nitrous acid (or rather of nitrososulphuric acid) and of nitric acid in the chamber-acid are so small that its quantitative estimation by the usual method is very inaccurate, especially as a number of impurities interfere with the accuracy of the process. In practice, however, a simple and rapidly made *colorimetric test* with ferrous sulphate is sufficient for the purpose, and is described below.

When a solution of ferrous sulphate is poured upon the drip- or chamber-acid contained in a test-tube so that the liquids are not mixed, a yellow ring is formed at the point of contact, if traces of the higher nitrogen oxides are present.[1]

[1] The customary brown-ring test for nitric acid occasionally gives very erratic results. These are traced to insufficient rapidity in the reduction of nitric acid. The defect can be most readily remedied by the addition of hydrochloric acid, a drop of which (4N) is introduced previously to the addition of sulphuric acid. The brown coloration is produced immediately. The presence of 0·5 mg. of potassium nitrate in 2 c.c. of solution can be detected with certainty. The limit of applicability of the method lies at about 0·2 mg. if control solutions are used to obviate the disturbance caused by the formation of yellow solutions of ferric chloride.

The oxidation of ferrous sulphate in solutions containing nitric and hydrochloric acids appears to proceed in such a manner that the acids first react with one another, and that the chlorine and nitrosyl chloride thus produced convert the ferrous into the ferric salt. The oxidation of ferrous sulphate by nitric acid, which occurs at high concentrations of nitric

With more nitrogen oxides the ring becomes darker; with still more, the whole ferrous sulphate solution assumes a deep brown or black colour. In this case, effervescence readily sets in, the liquid gets hot, and the dissolved nitric oxide, to which the black colour is due, is driven off by the heat. With some practice, and always working exactly in the same way, it is quite possible to get a good idea of the percentage of nitre in the chamber-acid by its appearance under the above conditions. The testing for a set of four chambers can be carried out in this way:—A stand containing eight ordinary test-tubes is once or, preferably, twice a day taken to the chambers, and the tubes half-filled with samples of the drip- and bottom-acids of each chamber. At the same time, the strength of each sample is taken by the hydrometer, and a note made of them. The acid-samples are then tested, at any convenient place, by carefully pouring on to each about half an inch of a concentrated solution of ferrous sulphate, which need not necessarily be free from ferric sulphate. By looking at the colours produced thereby, in their succession from chamber to chamber, by comparing the drips and bottom-acids, looking at the strengths recorded, and taking into account the colour and temperatures of the chamber-gas, a fairly good idea of the process going on in the chambers is obtained. This should be completed by an estimation of the sulphur dioxide in the burner-gas and of oxygen in the exit-gas, and also by testing the nitrous vitriol, etc., as described in the next chapter.

The following rules may be laid down for the *reactions with ferrous sulphate which the various samples of acid from the chambers and drips ought to show owing to their nitre content.* Generally speaking, all drips ought to show more nitre than the corresponding chamber-acids. The former represent the process going on in the atmosphere of the chamber, whilst the latter should act upon the nitre by their greater dilution, and actually do so. The *bottom-acid* of the *first or leading-chamber* ought not to show any nitre whatever. If it does so, it is a strong ndication that the supply should be reduced. (It must

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and sulphuric acids or at elevated temperature in the absence of hydrochloric acid, does not occur to an appreciable extent under the experimental conditions.—Carl Faurolt (*Ber.*, 1923, 56, (B) 337-341; *J. Chem. Soc.*, 1923, pp ii, 179).

be borne in mind that a slight quantity of nitre, which can be detected by finer tests, is nearly always present even in the first-chamber acid, but the rough test described above ought to show either none at all or very little.) First it must be ascertained if the drip of this chamber also shows any nitre. If it does not, it must be inferred that there is too little steam in the chamber, and that consequently the nitrous acid has been absorbed by the chamber-acid. Generally, this will be confirmed by both drip- and bottom-acids being too strong, and then *more steam* must be given. If, however, *both* samples from the first chamber show nitre, some of the latter must be cut off, unless the supply has just been increased because the last chambers did not show enough. In this case, the supply of nitre cannot be cut down till the last chambers have quite recovered.

Sometimes the acid of the first chamber smells of sulphur dioxide. If this is the case to any appreciable extent, there is a deficiency of nitre in that chamber.

The *middle* chambers ought to show a faint reaction for nitre in the bottom-acid and a stronger one in the drips. The *last* chamber should always show a moderately strong reaction in the bottom-acid and a very strong one in the drips. In this case, also, a deviation from the rule may proceed from various causes. For instance, the last chamber may be pale, and yet its bottom-acid may give a strong nitre-reaction. This may happen if there is too much or too little steam in this chamber. If the bottom-acid is too strong owing to the want of steam, it will dissolve too much nitre. If, however, there is too much steam present, the result will be the same as that which, in chambers working without an absorbing-tower, is purposely caused: nitric acid will be formed and will dissolve in the bottom-acid. Both faults are easily avoided if the last chamber is kept between 90° and 100° Tw. Sometimes insufficient draught may cause these faults. If, on the contrary, the last chamber still appears red, and the drips still show nitre, but the bottom-acid none, it is an indication that the supply of nitre must be instantly increased, otherwise the chamber itself will soon become pale. If both indications appear together, viz., a pale chamber and a diminution or weakening of the nitre in the drip, the trouble might still be due to an excess of

steam ; but this will rarely happen, as that chamber does not get much steam. Three other explanations offer themselves—too little draught, too much draught, or too little nitre. Insufficient draught is most easily confirmed by estimating the oxygen in the exit-gas ; too much draught, by estimating the sulphur dioxide in the burner-gas. Where no gas-analyses are made, the external indications previously mentioned for judging the draught are taken into account, but these are far more deceptive than gas-analyses. When the draught is insufficient, the nitric oxide does not meet enough oxygen for its oxidation ; it is colourless, and, owing to its insolubility in strong vitriol, it is altogether lost. This condition will be recognised by the appearance of red vapours when the gas comes out of the chimney, as the nitric oxide is oxidised by the atmospheric oxygen, whilst the chambers themselves, where oxygen is missing, become pale. Where there is too much air present, the nitrogen acids are carried away mechanically, and in this case also the chambers lose their colour ; at the same time, sulphur dioxide goes away, as it has not time to be oxidised.

Insufficient formation of sulphuric acid in the chambers, from other causes, such as want of nitre or the entrance of air through chinks in the chambers, which mechanically carries away gas, will frequently react upon the burners, since the draught from the burners towards the chambers is diminished by the insufficient condensation of gas. Then all the conditions which are caused by very bad draught in the burners, especially incomplete burning, will appear. In this case, as much nitre as possible must be given in order to force a better formation of sulphuric acid, and, if necessary, the burner-charges should be diminished.

If the last chamber becomes pale, the draught being in order, and if its acid shows little nitre, the trouble is due to want of nitre, and more of it must be introduced till the normal state has been restored. This will be confirmed by *testing the nitrous vitriol*, which will no doubt show a diminution of its nitre. Undoubtedly several circumstances often act at the same time, and make the process a complicated one. If, for instance, there is too little draught, so that, instead of N_2O_3, either NO or even SO_2 gets into the absorbing-tower,

not only will the draught have to be increased, but more nitre will have to be given, in order to make up for the loss. Similarly, when the nitre-gas has been mechanically carried away by an excess of draught (in which case, owing to its dilution, the Gay-Lussac tower cannot retain it entirely), not only will the draught have to be moderated, but more nitre will have to be introduced till everything is in order again.

An *excess of nitre* is detected by the colour of the chambers becoming too dark, by the strong nitrous content of the acids, and by the Gay-Lussac acid showing the presence of nitric acid, consequent upon an excess of N_2O_4 in the last chamber.

Thus, in nearly every case, when anything goes wrong in the acid-chambers, an increased supply of nitre is at least temporarily necessary in order to restore the equilibrium, although the other two regulators, steam and draught, must always be taken into account at the same time. It is therefore very important that the possibility be afforded of temporarily introducing much more nitre into the chambers than is necessary in ordinary work, and every factory ought to possess facilities for doing this. If it is not possible to introduce, without danger to the chambers, as much nitre as the case calls for, then nothing remains but to diminish the burning of brimstone or pyrites for a time, and to allow the chambers to recover their normal state.

At some of the best-conducted works it is not considered sufficient to judge of the supply of nitre by the colour of the chambers, the testing of the drips, and so forth, but a system is introduced of constantly checking the amount of nitrous vitriol supplied to the Glover towers and its strength, and also the amount of fresh nitre or nitric acid introduced compared with the amount of sulphur burnt, in order to keep the quantity of nitre present in the chamber as constant as possible.

It is advisable to keep records of the days' workings, and specimen of the forms used for the *tower* system is illustrated below (Fig. 148). Similar forms can easily be arranged for the ordinary *chamber* plant.

Another system introduced by the writer into several works is illustrated in the *Alkali Report*, No. 56, for 1919, p. 16.

Jacob Lutjens (B. P. 6617 of 1914) describes a process for automatically maintaining constant reaction in the chamber-

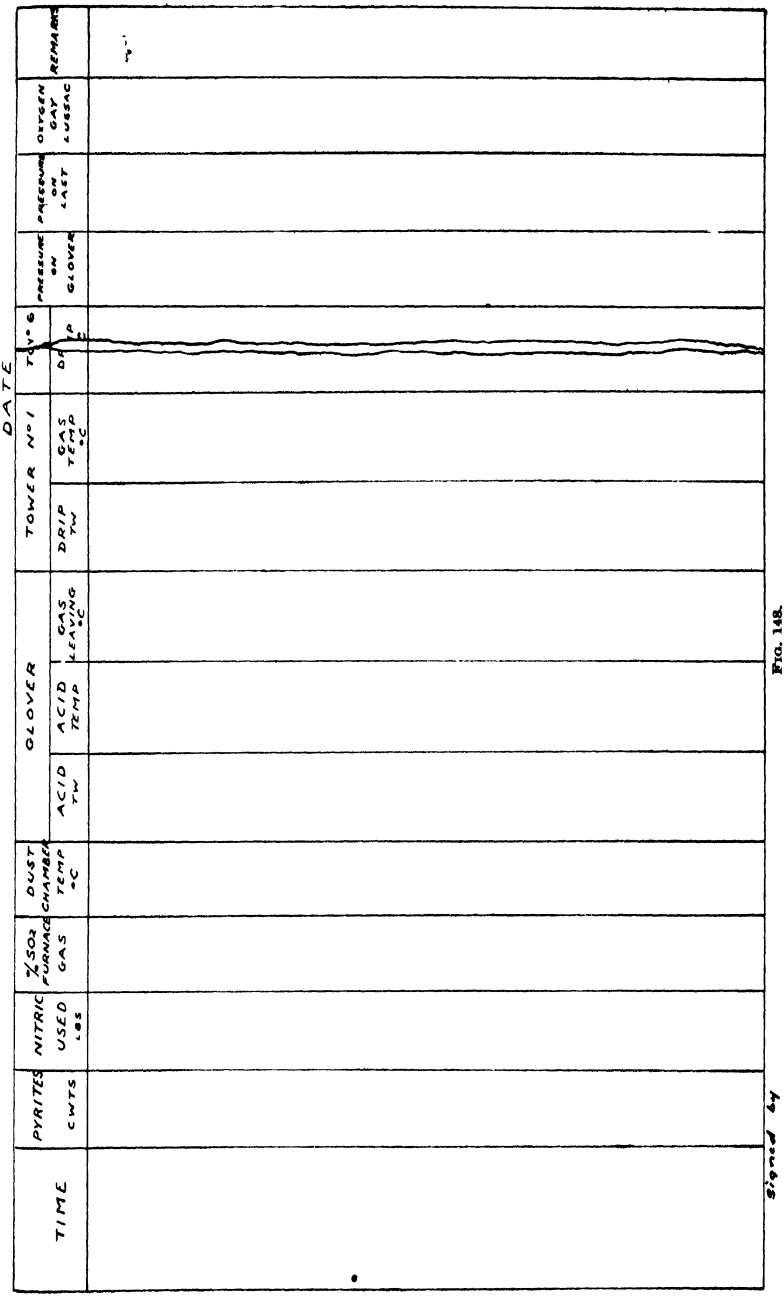
DATE
TIME
PYRITES CWTS
NITRIC USED Lbs
% SO2 FURNACE GAS
DUST CHAMBER TEMP °C
GLOVER
ACID TW
ACID TEMP
GAS LEAVING °C
TOWER N° 1
DRIP TW
GAS TEMP °C
TOWER N° 6
DRIP °F
PRESSURE ON GLOVER
PRESSURE ON LAST
OXYGEN GAY LUSSAC
REMARKS
Signed by

FIG. 148.

process by a device which regulates the supply of nitre to the system, the operation being controlled by a thermometer fitted in the apparatus. When the temperature in the chamber rises, the device is automatically closed or throttled, and when the temperature falls, it is opened.

According to the *Chemical Trade Journal*, 1923, **72**, 597, the problem of regulating automatically the amount of oxygen-carrier supplied to chamber-plants for the manufacture of sulphuric acid so as to safely reduce the amount of material consumed to a bare minimum has always been an attractive one, but it cannot be said that, up to the present, complete success has attended the efforts of those attempting its solution. The most promising of the methods proposed has been that based upon the temperature variations in the first chamber, a valve being closed electrically as soon as the temperature rose above the average level, and opened when the temperature fell. Unfortunately, the fundamental assumption upon which this method is based—namely, that in a system of chambers functioning normally the current of SO_2 and SO_3 is practically constant, and that a fall in temperature must thus indicate impaired oxidation conditions—does not take into account the occasional accidental but inevitable diminutions in the supply of sulphur gases. An increased amount of oxidising agent would then be supplied at a moment when really a reduced amount was necessary. An ingenious apparatus has, however, just been described by a French chemist, K. Warming,[1] which would seem to surmount this difficulty and to render automatic control entirely reliable. The new apparatus, which has been named "the oxyregulator," is based on the principle that in any system of sulphuric-acid chambers there exists an optimum temperature difference between the gases entering the first chamber and those leaving the last, and although circumstances may cause variations in the actual temperature of entry to the first chamber, yet the difference mentioned will always remain constant whilst the plant is functioning efficiently. Two electric thermometers are placed respectively in suitable positions in the first and last chambers. The thermometers are connected through two resistances to a galvanometer, the whole

[1] *Chimie et Industrie*, 9, 671-3, Assignor to Aktieselkab Dansk Svorlsyre- og Super-Phosphat-Fabrik (B. P. No. 199004).

circuit being arranged on the principle of the Wheatstone bridge, with the result that whilst the optimum temperature is maintained the pointer in the galvanometer remains steady. An appreciable increase or decrease in the temperature difference, however, will cause the pointer to move one way or the other, to make electrical contact, and by suitable electromagnetic devices to decrease or increase the amount of oxidising agent supplied. The device appears quite simple, and if the figures given by the authority quoted above are any indication, should be worthy of attention by British sulphuric-acid makers. In one test plant the amount of sodium nitrate consumed per 100 kilogrammes of sulphur burned was brought down from 3·92 to 3·06 kilos, and a reduction of 22 per cent. in the amount of nitrate is by no means negligible.

Proposals for modifying the Ordinary Way of supplying the Chambers with Nitre.

A proposal made by the Manufacture de Javel (B. P. 1752 of 1882) seems to be worthy of more notice than it has received. The nitre is not only introduced into the leading chamber, where the temperature may thereby become excessively high, but also to a small extent into the following chambers, where the temperature is sometimes too low. Even the acid for feeding the Gay-Lussac tower contains a little nitre, in which case no SO_2 escapes through the tower.

The United States Chemical Company, Camden, N.Y. (U.S. P. 325262 of 1885), injects nitrous vapours into the last chamber, after having first injected steam, in order to counteract any too strong reduction of the nitrogen oxides.

Starting from a contrary view, Benker (B. P. 1168 of 1895; *cf.* Kienlen, *Monit. Scient.*, 1895, p. 311) injects SO_2 (in the form of gas from the front of the first chamber) into the last chamber, in order to remedy the drawback, occurring in the "high-pressure work," that vapours of N_2O_4 are formed which, he believes, are not sufficiently absorbed in the Gay-Lussac tower. These are to be reduced to N_2O_3 by the SO_2 This is evidently the same principle as that involved in his former process (p. 199); the only difference is that he formerly injected the SO_2 immediately in front of the Gay-Lussac tower,

and that he now sends it into the last chamber. In regular work this process might act injuriously, but in cases where there is an excess of N_2O_4 it may do good.

The Swiss Société le Nitrogène (Fr. P. 404071) replaces nitric acid in the lead-chamber process by a mixture of nitroso-sulphuric acid and nitric acid, obtained by thoroughly saturating concentrated sulphuric acid, of 75 per cent. SO_3, with nitrous gases diluted to a great extent with air or an indifferent gas.

Macadam and Walker (B. P. 103877 of 1917) arrange one or more towers or structures, lined with lead and packed with acid-resisting material, between the Glover tower and the first of a series of lead-chambers, and a solution of sodium nitrate is sprayed into the gases as they pass through the tower or towers.

At the bottom of each tower, means are provided for drawing off the denitrated solution.

A convenient size of tower is 9 ft. to 12 ft. high by 4 ft. in diameter.

Temperature of the Chambers.

At every sulphuric-acid works the temperature of the chambers is a subject of constant observation on the part of the attendants, and it is generally understood that the regular and economical working of the process is intimately connected with keeping the temperature at any given point as constant as possible. The most suitable temperature differs in different parts of the same set of apparatus, and varies considerably in analogous parts of the apparatus at different works. The care with which the observations of temperature are made certainly varies very much. *Thermometers* should be fixed in several parts of the chambers, generally near the "drips" (p. 102), and their readings regularly recorded. In France and particularly in England this has up to the present been neglected, and even in large and otherwise very well managed works chamber-thermometers were frequently not found. It was often thought sufficient to test the temperature of the chambers by putting the hand upon the lead. It is hardly necessary to say that the latter plan is decidedly faulty, and the small expense and

trouble of applying and using thermometers should not be avoided.

This is independent of the question, whether a certain temperature is the theoretically best for the process of sulphuric-acid making or not, and whether this is the *cause*, or the *effect*, of the economical working of the chambers; for there is no diversity of opinion as to the fact that all causes leading to a faulty process act either directly or indirectly on the temperature of the chambers, and that the observation of the latter is one of the most important guides for judging of the proper working of the acid-making process.

Considerable diversity of opinion exists concerning the *best temperature for the chamber-process*, but there is no doubt as regards some general facts. The temperature of every chamber diminishes from front to back, and naturally that of the last chambers more than the first. All these differences in the normal process ought to be constant. The first chamber will be generally so hot, say 50° to 65°, that it cannot be touched by hand for any length of time.[1] In the absence of any cooling-apparatus, Glover tower, etc., the heat becomes so great that the lead cannot be touched with impunity, and in that case the chamber will not last very long. The temperature of the second chamber is generally about blood-heat; thermometers with their mercury-vessels inside the chambers show from 40° to 60°. The third chamber, if it be the last, will outwardly show little or no difference in temperature from the surrounding atmosphere; inside, its temperature will vary from 40° to 30° and even lower.

In normal circumstances the temperature of the first (leading) chamber will have a direct relation to the quantity of work put upon the system. With an allowance of 20 cub. ft. of chamber-space per lb. of sulphur, the normal temperature is, as stated before, from 50° to 60°, or at most 65°, whilst with 15 or 12 cub. ft. per lb. of sulphur, it is 80° at the inlet and rises to 90° or 95° further on. Even at the outlet it is still 15° or 20° above the temperature of the surrounding air.

Benker considers a difference of 10° between the inside and outside temperature at the last chamber a mark of excellent work; 18° or 20° should never be exceeded. He fixes a

[1] See *infra* for plants working in the Tropics.

thermometer on the outside as well as one inside, a course which is recommended.

The temperature of the chambers depends upon various factors. It is raised by the heat of the burner-gases and by that of the steam introduced, and also (to a far greater extent) by the chemical reactions of the acid-making process; sometimes, in hot countries and in unprotected chambers, by the heat of the sun. Part of this heat is withdrawn by radiation from the thin and quickly conducting leaden walls of the chamber, and also by the removal of the heat contained in the escaping gas and in the acid drawn off. The loss of heat by radiation will vary according to the season, to the wind, etc., but, of course, it will be much less with chambers enclosed in buildings than with those exposed to the weather. Since, for a given time, both this influence and the heat brought in by the burning-gases and withdrawn by the exit-gases and the acid manufactured, vary but little, the inner temperature will practically be governed by the intensity of the chemical reactions.

The facts now stated prove that *frequent observations of the temperature of the chambers are of great importance for the proper management of the process.* Although the temperatures at the various parts of the apparatus show very great discrepancies at different works, they are almost constant in the same set of chambers, so long as everything is in good working order. For this reason any considerable rise or fall of the chamber-thermometer, to the extent of say 5°, is a certain sign that there is some irregularity which should be remedied. This indication is all the more valuable as it is instantly observed without requiring any tests or loss of time, and it is accessible to any ordinary workman without the aid of a chemist.

A. O. Jones[1] also considers that the variations in the temperature of the gases at various points of the chamber-plant are the best guide to the course the reaction is taking. Since the rise in temperature increases the velocity of reaction, but decreases the yield, the question naturally arises as to what is the optimum temperature at which the gas mixture should enter the first chamber. As a general rule the gases should emerge from the draught-pipe at a temperature of

[1] *Chem. Tr. J.*, 1921, 69, 184.

about 55°, and as a good Glover tower delivers the gas mixture at a temperature of about 88°, the draught-pipe from the Glover to the chamber should be long enough to bring about the necessary cooling. Too long a draught-pipe would cool the gas to such an extent that the velocity constant would become very low, and on reaching the chambers the reaction would be slow in commencing under its new volume conditions. Too short a draught-pipe sends the gases into the chamber at a high temperature, causing an apparently vigorous action, but as the equilibrium constant is now rapidly diminishing owing to the high temperature, the yield is correspondingly less.

Maudsley[1] gives the temperatures existing in a plant working in the Tropics.

CONDITIONS IN WINTER.

	1.	2.	3.	4.	5.	6.	7.
Temperature of chambers, 11.30 A.M.	70°	62°	40°	61°	..	38°	36°
Temperature of chamber-acid . .	32°	28°	26°	30°	...	28°	29°
Density of chamber-acid Tw. . .	129°	117°	118°	135°	...	120°	117°

Temperature of atmosphere, 11.30 A.M., 26°.
Temperature of Gay-Lussac exit, 11.30 A.M., 31°; barometer, 29·4.
Yield of acid on sulphur burnt, 91·4 per cent.

CONDITIONS IN SUMMER.

	1.	2.	3.	4.	5.	6.	7.
Temperature of chambers, 11.30 A.M.	74°	...	57°	68°	48°	39°	...
Temperature of chamber-acid . .	33°	...	30°	32°	30°	29°	...
Density of chamber-acid Tw. . .	114°	...	119°	127°	112°	118°	...

Temperature of atmosphere, 11.30 A.M., 29°.
Temperature of Gay-Lussac exit, 11.30 A.M., 37°; barometer, 29·4 in.
Yield of acid on sulphur burnt, 86·60 per cent.
Chamber-space (62,152 cub. ft.), 9·5 cub. ft. per lb. of S.
Brimstone gas average, 10·9 per cent. SO_2; 8·8 per cent. O.
Pyrites gas average, 8·5 per cent. SO_2; 7·8 per cent. O.
Chamber-exit, 10·26 per cent. O, and 3·30 grains SO_2 per cub. ft.

At a chamber-plant in West India of which the writer

[1] *Chem. Tr. J.*, 1921, **30**, 133.

had charge, the following temperatures and strengths were found in a set of the three chambers (on low output).

Sulphur was burned and water sprays were in use.

No. 1 chamber 120° Tw. drip, 74° C. middle of chamber-side.
No. 2 ,, 116° ,, 62° ,, ,, ,,
No. 3 ,, 105° ,, 47° ,, ,, ,,

The temperature in the shade was from 26° in the night, to 39° towards noon. The average shade temperature during the whole year was 30°.

On the East coast at a four chamber-plant, the following strengths and temperatures were found :—

No. 1 chamber 128°-132° Tw. and 90° to 110° C.
No. 2 ,, 116°-120° ,, ,, 80° ,, 90° ,,
No. 3 ,, 106°-112° ,, ,, 60° ,, 70° ,,
No. 4 ,, 100°-106° ,, ,, 50° ,, 60° ,,

Brimstone was also used, but in this case, with steam in place of water sprays. The chamber-space was from 9 to 12 cub. ft. per lb. of sulphur per 24 hours.

Mention must now be made of an *abnormal state of things* which is sometimes observed, namely, a rapid sinking of the temperature of the first chamber, whilst that of the last chamber rises far above the proper degree. This is always accompanied by the colour of the gases getting paler, first in front, then also behind, so that even the last chamber may become quite grey. At the same time, there is a great deal of liquid condensing on the glass of the "sights." Ultimately the quantity of sulphur dioxide going away unoxidised may become so large that the nitrous vitriol within the Gay-Lussac tower is denitrated, and the escaping nitric oxide, on contact with the air outside, forms dense red clouds. This state of things is brought about by all the causes which disturb the proper process—want of water, want or excess of steam or of air. All of these tend to keep the process back, so that the first chamber does too little work and the last chamber too much. An examination of the composition of the gases at the inlet and at the outlet, and of the strength and nitrogen content of the drips, will lead to localising the cause of the disaster and admit of applying the proper remedy. In addition to other remedies, a fresh supply of nitre must usually be given, in order to get up the temperature of the first, and reduce that of the last chamber; that is, to bring back the maximum of production to its proper place in front

of the apparatus. Where it is impossible to get enough fresh nitre into the chambers, the pyrites-burners must be kept back, to diminish the amount of sulphur dioxide in the chamber atmosphere. The indications of the thermometer in the *last* chamber are very important. If the temperature rises above the normal point, the proportion of sulphur dioxide to that of the nitrous gases and steam is sure to be wrong, and should be remedied at once before more mischief is done.

Cooling the Chambers.—Pratt (U.S. P. 715142, 2nd December 1902) cools the chambers, towers, flues, or conduits by a cooling medium without bringing them directly into contact with the latter. He also cools the hot uncombined gases, which are then passed back again into the chamber.

Lagache (Ger. P. 144084; Fr. P. 350363) cools the gases from the hottest part of the chambers, especially for the "high-pressure style," by taking them out by means of a fan, passing them through a cooler and then back into the chamber.

Depth of Acid.

It is a general belief among practical men that the *depth of acid at the bottom of the chamber* influences the completeness and regularity of the chamber-process. In their opinion the best yield and the most regular work are only obtained by keeping a good stock of acid in the chambers, say 9 in. or more. On the contrary, a very experienced acid-maker, M. Delplace, emphatically denies that the process is improved by a great depth of acid. He was in a position to start a chamber (the sides of which were burnt to the bottom) without any acid at all. The drops could be heard to splash upon the lead as they fell, yet both the yield of acid and the consumption of nitre (1 part to 100 O.V.) were as favourable as in any other case. It must not be overlooked that a very great depth of acid diminishes the available chamber-space.

The writer is of the opinion that it is of great importance for the regularity of the chamber work to keep a good layer of acid at the bottom of the chambers. From his experience over a number of years on a plant burning pyrites, the nitre consumption invariably increased whenever the acid was at

a low level (some parts of the chamber-bottom only having a coating of lead sulphate), whereas when the depth of acid increased a few inches, the consumption of nitre was back to the normal figure.

General Remarks.

In checking the process it must never be overlooked that any one symptom may be due to various causes. For example, the acid may get weaker either by a falling-off in the production or by an excess of steam. The draught may be lowered by a smaller acid-production, by atmospheric influences, or by the gas-flues becoming stopped up with deposit. An insufficient conversion of sulphur dioxide into sulphuric acid may be caused by too weak or too strong a draught. The nitre may decrease in the chamber either through an excess of steam, which leads to formation of nitric acid, or through a deficiency of it, which leads to chamber-crystals dissolving in the bottom-acid. In both cases the strength of the acid falls off. Owing to the fact that in acid-making a certain effect may be caused by different circumstances, the management of chambers is not an easy task, but requires great judgment and experience.

Irregular Working. Loss of Nitre.

Having so far stated the conditions of the normal vitriol-chamber process, it would also be well to consider how the process may become anomalous, that is faulty, which would in every case lead to losses both of nitre and of sulphur compounds.

Sometimes "free" nitrogen peroxide appears in the last chamber (never in the others). It has been proved by Lunge and Naef[1] that this happens when the supply of nitre is abnormally large, and does not depend on a larger or smaller excess of oxygen, as there is always far more than enough of this gas present. In this case the formation of sulphuric acid is finished before the proper time. There is very little SO_2 in the last chamber, and the nitrous anhydride, which cannot

[1] *Chem. Ind.*, 1884, p. 8.

be again taken up by the chamber-gases, is completely dissociated into NO and NO_2, the former also being oxidised to NO_2. The NO_2 where it touches the chamber-acid dissolves in it and forms both nitrous vitriol and nitric acid. Most of the NO_2, however, passes into the Gay-Lussac tower; and as the size of this apparatus is only calculated to meet normal requirements, it cannot retain all the nitrous gas, but emits a good deal of it into the air in the form of ruddy vapours, with a corresponding loss of nitre.

Far more serious are the consequences of a *lack of nitre*. In this case, the formation of sulphuric acid is too slow, and there is too much SO_2 in the back part of the chambers, which causes a denitration of SO_5NH in the *wrong* place. A large amount of NO is formed, the chambers turn pale yellow, or, in extreme cases, grey, and the temperature is either too high or too low for proper working. Owing to the relative excess of water the formation of the intermediate compound SO_5NH is greatly impaired, and the NO now forms, with oxygen and water, nitric acid, which sinks down to the bottom and dissolves unchanged in the chamber-acid, and is thus withdrawn from the chamber-process. This acid will not "show nitre" in the sense used by practical men—that is, it does not give out orange vapours on addition of water, because it contains little SO_5NH, but for all that it may contain so much nitric acid that the chamber-lead is seriously attacked. The nitric oxide, on passing into the Gay-Lussac tower, is not absorbed at all by the sulphuric acid, the excess of inert nitrogen preventing its reaction with SO_2 and O, and at the top both NO and SO_2 escape, thus causing a double loss. A third source of loss is the formation of nitrous oxide, N_2O, for which the conditions now exist to a much greater extent than normally (see below). All this leads to a bad yield of sulphuric acid from the start and to a great loss of nitre, and as this instantly reacts upon the chamber-process, the floating quantity of oxygen-carriers being diminished at a progressive rate, it is no matter of surprise that things get from bad to worse. Every practical man knows, and Eschellmann has proved it in detail,[1] that when there has been lack of nitre from any cause whatever, it is necessary to introduce *several times* the amount

[1] *J. Soc. Chem. Ind.*, 1884, p. 136.

originally required in order to remedy the "disease" of the chambers.

Causes of the Loss of Nitre.—It is a notable fact that in no case whatever is the recovery of the nitrogen oxides, employed in the manufacture of sulphuric acid, complete. Even with the best nitre-recovery and denitrating apparatus, and under the best possible management, the loss is rarely below 1·7 parts of $NaNO_3$ to 100 of sulphur burnt, and it is nearly always higher than that, 3 parts of $NaNO_3$ probably indicating the present average. The causes of this loss of nitre are various, and may be distinguished as mechanical and chemical losses. *Mechanical losses* are those caused by incomplete absorption of N_2O_3 or N_2O_4 in the Gay-Lussac tower by the removal of the nitrous acid contained in nearly every description of acid withdrawn from the process for sale or use, and by any accidental leakages from working-doors, chambers, etc. *Chemical losses* are those caused by the reduction of the nitrogen oxides below the point where they can be reoxidised or absorbed in the Gay-Lussac tower. Generally, this chemical loss is ascribed to a reduction to nitrous oxide, or even elementary nitrogen, or (by Raschig) to ammonia; but the last mentioned, according to Raschig's own statement, is found only in quite exceptional circumstances and need not be taken into account for ordinary purposes. That a reduction to N_2O does take place under certain conditions (excess of SO_2 and undue local excess of water) has been proved by R. Weber and by Lunge (p. 259 of Vol. I), and it is probable that such conditions do exist to a certain extent in every vitriol-chamber. They exist, however, to a less extent in the Glover tower than elsewhere, though it was at one time believed that the loss took place there (p. 206). Up to the investigation by Inglis (mentioned below), it was, however, entirely uncertain what proportion the mechanical and chemical losses bore to each other. The most extraordinary discrepancies existed in this respect. Some chemists asserted that the mechanical loss, more especially that caused by incomplete action of the Gay-Lussac tower, is by far the most potent cause of loss of nitre;[1] others were of the contrary opinion. It seems useless to go into the detail of this contro-

[1] Lunge and Naef, *Chem. Ind.*, 1884, p. 11; Benker; Sorel, *Z. angew. Chem.*, 1889, p. 279.

versy here, as no conclusive proof was given either way, and we will only quote some of the other papers bearing on this question: Hurter, Davis, Jackson, Mactear, Cox, and Lunge, in vol. xxxix. of the *Chem. News* (pp. 170, 193, 205, 215, 227, 232, 237, 249); Eschellmann (*J. Soc. Chem. Ind.*, 1884, p. 134); Hamburger (*ibid.*, 1889, p. 167). An important loss of nitre is caused by the *coke-packing* of the Gay-Lussac towers. Lunge long ago (*cf.* p. 152) proved that the coke reduces any N_2O_4 getting into the Gay-Lussac acid, so that the nitrous vitriol issuing at the bottom contains only N_2O_3. He has shown (in the same place) that nitrosulphuric acid itself is reduced by coke, NO escaping. This action is greatly increased by a higher temperature, and this may be one of the reasons why it is expedient to cool both the gases and the absorbing acid as much as possible; it also seems to favour the use of Gay-Lussac towers containing a non-reducing packing (p. 234).

Concerning the formation of *nitrous oxide*, we have seen on p. 259 of Vol. I that this will happen if NO (or N_2O_3) meets an excess of SO_2 *in the presence of water* or of very dilute sulphuric acid. The reduction may then take place according to the equation—

$$SO_2 + 2NO + H_2O = H_2SO_4 + N_2O.$$

It is not impossible that, under specially unfavourable circumstances, the reduction may proceed even as far as the formation of elementary nitrogen or of ammonia, but this evidently happens only quite exceptionally and to an altogether insignificant extent. Most chemists assume that the formation of N_2O occurs to a small extent, even in normally working-chambers, at places where water and sulphur dioxide are locally in excess. Actual proof of this, by showing the presence of N_2O in chamber-gases, could not be given formerly; in fact, the known analytical methods would hardly permit this.

'All the more important is the work done by Inglis,[1] who, at the suggestion of Ramsay, carried out the fractional distillation of liquefied chamber-acid gases, which were cooled to about $-185°$ by means of liquid air. By this means, and by repeated rectifications at suitable temperatures, the substances

[1] *J. Soc. Chem. Ind.*, 1904, p. 634 *et seq.*

present could be divided into the following fractions: (1) nitrogen and nitric oxide; (2) nitrous oxide and carbon dioxide; (3) sulphur dioxide; (4) nitrogen peroxide and sulphuric acid. The fractions were measured and then analysed in the ordinary way. The flue-gases at the Silvertown factory were tested in this way, 284 l. being treated altogether, with fairly constant results. An extremely small quantity of nitrous oxide was found, about 0·002 per cent. The conclusion reached from this is that the "chemical loss" of nitre is negligible so far as nitrous oxide is concerned. The gases contained about 0·04 per cent. nitric oxide and about 0·03 per cent. nitrogen peroxide. The total loss of nitre being 0·1 per cent., 70 per cent. of this loss is accounted for by the mechanical loss in the form of NO and NO_2, and its amount depends upon the efficiency of the Gay-Lussac tower.

In the discussion following the reading of that paper, all the speakers agreed that the "chemical loss" of nitre in the ordinary working of the chambers was altogether insignificant. Divers especially pointed out that it is now unnecessary to assume the formation of the hypothetic compounds suggested by Raschig (*cf.* p. 258 of Vol. I).

Later Inglis[1] describes very careful experiments made by his methods with flue-gases at a factory, which led to the same result, viz. that only very small quantities of NO_2 and N_2O_2 are reduced to N_2O in the chambers. About 50 per cent. of the total loss of nitre is owing to incomplete absorption of NO_2 and N_2O_3 in the Gay-Lussac tower, and Lunge's view in that respect is the correct one. In his concluding paper[2] he sums up his results as follows: (1) the amount of nitre lost as N_2O is less than 10 per cent. of the whole loss; (2) a considerable proportion is lost as nitrogen peroxide and nitric oxide, the relative proportions of these two substances depending upon the escape of SO_2; (3) there is a possible reduction to nitrogen.

It is a fact that, by enlarging the Gay-Lussac towers beyond the size formerly used, the loss of nitre can be greatly reduced, and mention of this has been made before (p. 147): but it would seem as if the practical limit in that respect had been

[1] *J. Soc. Chem. Ind.*, 1906, p. 149.
[2] *Ibid.*, 1907, p. 670.

reached when the Gay-Lussac towers, with coke-packing, have a capacity of 2, or at most of 3, per cent. of the chamber-space. Any further addition of absorbing-power causes an insignificant diminution in the loss of nitre. The cause of this is no doubt, as pointed out by Bailey,[1] that the coefficient of solubility of N_2O_3 in sulphuric acid is immensely reduced by its enormous dilution in the exit-gases with oxygen and nitrogen, and that therefore a complete absorption of N_2O_3 is an impossibility. Sorel (in the place quoted above) comes to a similar conclusion by observation and calculation, and shows that, in a special instance, the exit-gases were bound to carry away nitrous acid equivalent to 3·09 per cent. of $NaNO_3$ to 100 of sulphur—that is, more than the best working factories consume altogether—and Lunge's observations have accumulated convincing material for such conclusions. It is true that direct analysis of the exit-gases in many instances fails to account for more than a portion (say a third or even a quarter) of the nitre lost; but it cannot be denied that this may simply be an unavoidable fault in the analytical methods used, as it is extremely difficult, or rather impossible, to retain in absorption-tubes all the N_2O_3 or N_2O_4 when it is diluted with ten thousand or more times its volume of other gases. Any reasoning based on the analysis of exit-gases is therefore extremely unsafe, if it is intended to prove that the loss from that source is sufficiently small to dispense with the necessity of assuming a considerable chemical loss.

It is even more difficult to estimate NO in excess over the proportion $NO+NO_2$ when it is mixed with a very large excess of other gases, and hence the conclusions mentioned above are all the more uncertain. The loss of NO may be reckoned partly among the mechanical and partly among the chemical losses. The former is the case when any NO which has come from the chambers themselves has only mechanically escaped oxidation to NO_2 and consequent absorption in the Gay-Lussac tower; but it must be reckoned as chemical loss if the NO has been formed within the Gay-Lussac tower itself by some reducing action on nitrous vitriol. It has been seen that such an action may take place in the presence of an accidental excess of SO_2; but this happens only in exceptional cases, although it is possible that the SO_2, always present in

[1] *J. Soc. Chem. Ind.*, 1887, p. 92.

exit-gases even with the very best work, in spite of its very slight quantity, exerts a certain reducing-action in the Gay-Lussac tower. The sudden and exceedingly high losses of nitrate of soda which occur from time to time, both by the tower and chamber-process, are ascribed to the presence of fluorine or silicon fluoride in the gases from the pyrites-burners.[1] These combine with nitric oxide and nitrous anhydride and interfere with their action as oxygen carriers. The presence of ferrous oxide or sulphide in the flue-dust also results in a loss of nitrate, as the ferrous sulphate produced in the Glover tower reduces nitrous anhydride in the Gay-Lussac tower to nitrogen. The presence of arsenic is not considered to cause a loss of nitrate.

Distribution of Gases and Rate of Formation in the Various Parts of the Chambers.

The following observations and considerations possess far more than a merely theoretical interest. They are intimately connected with the questions:—Which is the best shape for a vitriol-chamber? Should contact-surfaces for the better condensation of the acid be provided, in addition to mere chamber-space? What are the real duties performed by the various parts of a set of vitriol-chambers, and can these duties be performed in a more advantageous way? and so forth. These questions have been treated at considerable length in preceding chapters, and they also influence the theory of Sulphuric Acid Manufacture (see below).

The experiments made by H. A. Smith, and recorded in his pamphlet, *On the Chemistry of the Sulphuric Acid Manufacture*,[2] are entirely untrustworthy, as pointed out in the first edition of Lunge, p. 285 *et seq.* His conclusion, that the chief portion of the acid made in the chambers is produced and is condensed close to the surface of the acid already formed in the chambers, has not been confirmed by any other observer, and it is also in direct contradiction to his own analyses of the gases. Hasenclever[3] fixed lead dishes in several parts of his

[1] G. Rosendahl (*Chem. Zeit.*, 1922, 46, 1036; *J. Soc. Chem. Ind.*, 1923, p. 11A). [2] London, 1873.

[3] A. W. Hofmann's *Report on the Vienna Exhibition*, 1, 178.

chambers, covering them over at a height of one foot, and thus found that about the same quantity of acid was formed all over the chamber. His conclusion certainly cannot be proved definitely in this way, since the dishes act as contact-surfaces, as will be shown later.

Mactear[1] has published an extensive series of observations on the distribution and condensation of the gases in the vitriol-chambers. They are of no use for settling the point at which part of the chamber the principal formation of the acid takes place, as they were based on a wrong principle, viz. that of observing the quantity of acid condensed on trays of a certain surface. It has been frequently shown, even by Mactear himself in the same paper, that solid (or liquid) surfaces within the chambers have an intense condensing action upon the acid, which means that the mist of impalpably small drops on striking such surfaces condenses into larger drops and collects upon the trays; hence the quantity of acid running away from the trays is not that made in the space above them, but represents a very much larger quantity, made partly, and possibly to the greatest extent, at some distance from the place where the tray is located.

The unreliability of the plan of testing the amount of sulphuric acid formed in a special part of the chamber by means of collecting-trays has been very clearly shown by Naef.[2] The condition supposed by previous observers to exist was that the trays collected all the acid formed in the vertical space above them. If it were so, very little acid would be found when the tray is provided with a cover. If, however, the drops fall down in a slanting direction, some acid will be found, and its quantity ought to vary in proportion to the distance between the tray and the cover. This is not the case, however. Naef placed within the chamber on one side an open tray, and on the other side a tray with a wider cover suspended over it at a variable distance. The result of weekly averages was that the tray with the cover 12 in. above it collected exactly as much as the open one, and even when the cover was only 4 in. above the tray the acid collected was nearly as much as with the open tray. Repeated observations entirely confirmed this result. This surprising phenomenon cannot be explained by a slanting fall of the drops, for it would require the fall to take

[1] *J. Soc. Chem. Ind.*, 1884, p. 224. [2] *Chem. Ind.*, 1885, p. 287.

place at an angle of 20°, which could not be produced even by the most violent movement within the chamber, a movement far above anything which really exists. There is no explanation other than one to which a very large number of former observations, including those of Mactear, irresistibly lead—that the sulphuric acid, when formed, exists in the shape of a very fine mist which is very slowly deposited in the form of a rain, and is carried forward by the gases for long distances, but is suddenly condensed when it strikes against solid [or, perhaps, liquid] surfaces. Therefore the acid is not deposited in a liquid state where it is formed, but further on, in very different quantities according to the surfaces it meets. Hence arise the apparent contradictions between the results of gas-analyses and those of measuring the acid condensed on trays. The latter mode of observation is utterly worthless for deciding the question of the progress of the chemical reactions; this progress must undoubtedly be studied by gas-analyses. This last method presupposes that the gases in any special transverse section of the chamber are almost, although not absolutely, uniformly mixed; and it has been proved that this is so by the results of Lunge and Naef (see Lunge, fourth edition, p. 960), as well as by those of Mactear himself. The fact that nearly as much liquid acid is condensed on the trays near the top as upon those near the bottom of the chamber is easily explained by Abraham's theory of a spiral movement of the gases (see *ibid.*, p. 967), of which it is, indeed, a necessary consequence.

Hence, we cannot accept Mactear's conclusion that the principal part of the acid is made in the upper portion of the chamber. In fact, this does not agree with his own analyses of the chamber-gases, and it agrees even less with his further conclusion (p. 228 of his paper) that the principal condition is that of "having ample chamber-space, the form of the chamber not being so material." The argument that the sulphuric acid forming and falling rapidly towards the bottom of the chambers must displace the gases and force them to the upper portion is fallacious; for the volume of the acid forming is several hundred times less than that of the gases concerned in its formation, so that the above-mentioned action must be imperceptibly small.

Mactear's observations on the rate at which the acid is formed in different chambers of a set, are very interesting.

The following table shows the comparative condensation of acid in the six consecutive chambers :—

No. of chamber.	Acid made.	H_2SO_4 in acid made.	Excess water.	Per cent. of H_2SO_4 made in each chamber.
	Tons.	Tons.	Tons.	
1.	23·52	19·89	3·63	32·20
2.	22·59	18·68	3·91	30·26
3.	20·35	14·89	5·46	24·11
4.	10·23	4·35	5·88	7·04
5.	5·84	3·09	2·75	5·00
6.	2·19	0·86	1·33	1·39

The following table is also taken from Mactear's paper, and shows the comparative condensation in the chambers of various sets :—

Chamber or connection.	Per cent. of production.						
	Works.						
	a.	b.	c.	d.	e.	f.	g.
Chamber 1 .	31·50	34·1	33·8	63·9	38·7	53·9	32·0
,, 2 .	29·27	20·0	42·2	36·1	33·6	36·9	29·0
,, 3 .	18·71	19·7	22·6	..	12·9	9·2	17·5
,, 4 .	10·32	18·1	...	..	9·8	..	13·7
,, 5 .	6·45	7·3	..	..	3·4	..	5·4
,, 6 .	3·75	0·5	...	...	1·6	...	2·4
,, 7 .	...	0·3	...	...	...	.	...
Tunnels .	...	...	1·4	...	...	...	...
	100·00	100·0	100·0	100·0	100·0	100·0	100·0

Crowder [1] quotes the results obtained with gases taken from testing-holes in the connecting pipes :—

	Lump-ore kilns.		Dust kilns.	
	SO_2.	O.	SO_2.	O.
From Glover tower to No. 1 chamber	6·9	8·0	5·2	11·8
,, No. 1 to No. 2 . . .	4·4	7·5	2·4	11·8
,, No. 2 to No. 3 . . .	1·9	5·7	1·2	10·6
,, No. 3 to No. 4 . . .	0·4	6·1	0·6	10·2
,, No 4 to Gay-Lussac .	0·3	5·7	0·4	9·3

[1] *J. Soc. Chem. Ind.*, 1890, p. 302.

According to Maudsley[1] the production of acid in a chamber system working on sulphur and pyrites in the Tropics was as follows:—

No.	Capacity, cub. ft.	Production of acid per day in cwt. of 123° Tw.	Surface of lead per cwt. of acid, sq. ft.	Space per lb. sulphur per 24 hours, cub. ft.
1	11,600	34	98	13·2
2	19,733	62	91	12·4
3	26,000	80	89	12·7
Pipe column 216		4¼	131	2·0
4	27,000	46	157	2·0
5	11,733	3½	957	130·0

Probably the most extensive and complete investigation on the phenomena taking place in the vitriol-chambers has been made by Lunge in conjunction with Naef at the Uetikon Alkali Works near Zurich, where a set of chambers was placed at their disposal for this purpose during a period of several months.[2]

Only the summary of their findings is given here, and for further details the reader is referred to their original paper, or to Lunge's fourth edition, p. 960 *et seq.*

As their investigations were made on a plant working at 16 cub. ft. per lb. of sulphur per twenty-four hours, the conditions prevailing in a plant working intensively would probably give results varying very considerably from those enumerated, and further research would therefore be desirable and interesting.

A. *The nitrogen oxides present in the last chambers correspond essentially to the composition of nitrogen trioxide, this being accompanied in the first chamber by nitric oxide, NO.*

B. *Free nitrogen peroxide, being absent in normally working chambers, cannot take any essential part in the formation of sulphuric acid in the chambers.*

C. *The quantity of air sent into the chambers has no influence whatever upon the formation of free nitrogen peroxide,* which, on the contrary, is *exclusively* caused by an excess of nitre.

D. *The conversion of SO_2 into H_2SO_4 takes place very quickly as far as the middle of the first chamber; it then slackens very*

[1] *Chem. Tr. J.*, Jan. 1921, p. 133.
[2] *Chem. Ind.*, 1884, p. 5 *et seq.*

much, but is suddenly revived when the gases pass from this into the next chamber.

E. *All the experiments proved that the gases within the chamber are very quickly mixed up (whatever the cause of this may be), but that the mixture is not an absolutely uniform one; there is always more SO_2 in the central part of the chamber than at the outside, the top, or the bottom.*

F. *The gases travel in vertical layers, which are at right angles to the length of the chamber, from the front to the back end, but each single gaseous molecule describes a spiral line, the axis of which is parallel to the length of the chamber.*

This is, of course, only a general expression of the path of the gases within the chambers, and is modified locally by special circumstances; but it accounts for the approximate equality of the composition of the gases and temperatures observed in Lunge and Naef's, and even in Mactear's, experiments.

Improvements proposed for Acid-chambers in accordance with the Investigations described above.

Hartmann and Benker [1] accept this theory and base thereon their arrangements for producing the proper movement of the gases by means of a fan, placed at the end of the system, by which means they obtained a very strong "intense production." Th. Meyer [2] strongly contradicted their assertions.

Porter [3] made some experiments with a glass model chamber, from which he concluded that the gases should be admitted into the chamber at the bottom, and the steam at both ends, so that it would mix with the centre core of both incoming and outgoing gases.

Carbon Dioxide in Chamber-gases.

It is generally assumed by manufacturers that carbon dioxide exercises a very injurious action in the lead-chambers, and it is principally on this account that "coal-brasses" are not con-

[1] *Z. angew. Chem.*, 1903, pp. 861 to 869.
[2] *Ibid.*, p. 927.
[3] *J. Soc. Chem. Ind.*, 1903, p. 476.

sidered a good raw material for the production of sulphuric acid (p. 122, Vol. I). If this is really the case, it is all the easier to understand why the proposals for filling the lead-chambers with coke have been unsuccessful. The reason why carbon dioxide should be injurious is not yet clear. Some practical men assume that the CO_2 forms distinct layers, preventing the intimate contact of the gases with each other and with the bottom-acid; but, according to Lunge, there are no direct observations on this point, except in one case where blende containing a high percentage of carbonate was worked, when it was found by many gas-analyses that the carbon dioxide accumulated in the corners and other "dead" places, whilst the main stream of the gases contained much less CO_2. The writer has not found any difficulty in working the chamber-process with coal-brasses as the source of sulphur, even though the material contained a considerable percentage of carbonaceous matter. The nitre consumption did not exceed 1·0 per cent. on the O.V. made, when allowing 20 cub. ft. of space per lb. of sulphur per twenty-four hours.

The possible development of the chamber-process in the near future will be watched with interest. Considerable work has recently been carried out in Canada upon the application of *silica gel* in the adsorption of sulphur dioxide from gases containing small quantities of sulphur dioxide. From gases containing as low a percentage of sulphur as one, it has been found possible to recover the sulphur dioxide in a much more concentrated form. Supplying the chambers with sulphur dioxide of 20 to 30 per cent. has great possibilities.

Testing the Chamber Exits.

Apart from the ultimate check on the process afforded by frequent estimations of the yield of acid and the consumption of nitre, it is very desirable, and has even for some time past been required by law, to control the quantity of acids escaping from the vitriol-chambers into the atmosphere. So far as "low-level escapes" are concerned, for example, the gas blowing out of the pyrites-kilns, potting-holes, accidental leaks in the chambers, and so forth, it is not possible to estimate them directly; but it is just these kinds of escapes that are most

readily perceived, and although they may be very troublesome to those residing in the immediate neighbourhood, they very rarely amount to any considerable percentage of the sulphur burned.

It is very different with the gases escaping from the end of the whole system into the atmosphere, whether it be through a simple pipe, a Gay-Lussac tower, or the chimney. These "high-level escapes" may cause a serious manufacturing loss, and they may also amount to a real nuisance to the people living near the works, although in most instances only temporarily, and especially in unfavourable weather. Before the introduction of nitre-recovery apparatus, the loss both of the acids of sulphur and those of nitrogen must have been far more considerable than it is now, as the whole style of working inevitably tended in that direction. Nothing certain, however, can be stated with regard to this, as no observations on the acidity of chamber-exits were formerly made, and at present all well-arranged works recover their nitre. In this case, the losses will not be quite so serious, but they exist all the same, and to a greater extent than was formerly supposed.

Among the first who drew attention to the necessity of regularly testing the chamber-exits for their acidity were Mactear[1] and G. E. Davis.[2]

Control of the acids escaping from the chambers into the atmosphere has been made compulsory in England, since, in 1881, it was enacted by law that the total quantity of sulphur acids escaping from an alkali-works should not exceed 4 grains per cubic foot, expressed in terms of sulphuric anhydride, SO_3 (sec. 8 of the Act). With regard to nitrogen acids or nitric oxide, nothing is enacted, probably because the quantity escaping from acid-works is never so great as to cause a nuisance, but it is important for the manufacturer himself to know how much nitre he is losing in this form; moreover, in testing the chamber-exits it is but little additional trouble to include the nitrogen acids.

In Germany, by an Order in Council of 1st July 1898, the maximum amount of total acids in the exit-gases of works burning pyrites was fixed at 5 grams, from blende 8 grams per cubic metre, calculated as SO_3.

[1] *Chem. News*, 36, 49. [2] *Ibid.*, 41, 188.

The Alkali Reports show that the escape of acid gases from the exits of sulphuric-acid works is far below the maximum prescribed by the Act. The following are the average escapes (taken from returns from England and Ireland) calculated in grains SO_3 per cubic foot :—

1915 . . 1·137	1918 . . 1·225	1921 . . 1·06
1916 . . 1·269	1919 . . 1·206	1922 . . 1·22
1917 . . 1·342	1920 . . 1·130	

Two systems may be employed for controlling the acid escapes—either that of taking several separate tests through the day, or that of continuously aspirating some of the gas through a set of absorbing-apparatus, and measuring the quantity of gas passed through them.

The unreliability of the first system is too obvious to be enlarged upon, and it is hardly applicable at all to night-work. Hence, the continuous-testing system has been generally adopted, and at many works the apparatus invented by Mactear is used. His apparatus consists of a water-jet pump (of the type invented by Sprengel, but commonly called the "Bunsen pump") for aspirating the gases, a set of absorbing-tubes, and a gas-meter to measure the volume of the residual gases after absorption. The whole, including the cocks and connections, is enclosed in a locked chamber to prevent it being tampered with. The meter is fitted with an index so arranged that by observing the reading for one minute the rate of passage per hour is given by direct indication, so that the rate of aspiration is easily adjusted. Mactear at first proposed caustic soda and ammonia as absorbents, to be titrated for SO_2 with permanganate; but this would yield wrong results, far below the truth, as sodium sulphite is rapidly oxidised by the oxygen passing through the solution.

Mactear's apparatus is very efficient, but it is very costly, and any such delicate apparatus as a gas-meter is very liable to get out of order when in proximity to acid vapours. Hence, at most places cheaper and simpler forms of aspirators have been adopted. One of the simplest is represented in Fig. 149. It consists of two glass bottles I. and II. provided with india-rubber stoppers through which pass elbow-tubes (*a*, *b*) ending just below the stoppers, and others (*c*, *d*) reaching down to the bottom of the bottles. The tubes *c* and *d* are connected by a

rubber tube ; another tube connects either *a* or *b* with the absorbing-apparatus. One of the bottles, say I., is placed so that its bottom is raised above the top of II. If *b* is now connected with the absorbing-apparatus, and the air is sucked from *a* for a moment, the siphon formed by *c*, *d*, and the rubber tube begins to run, gas being aspirated through *b*.

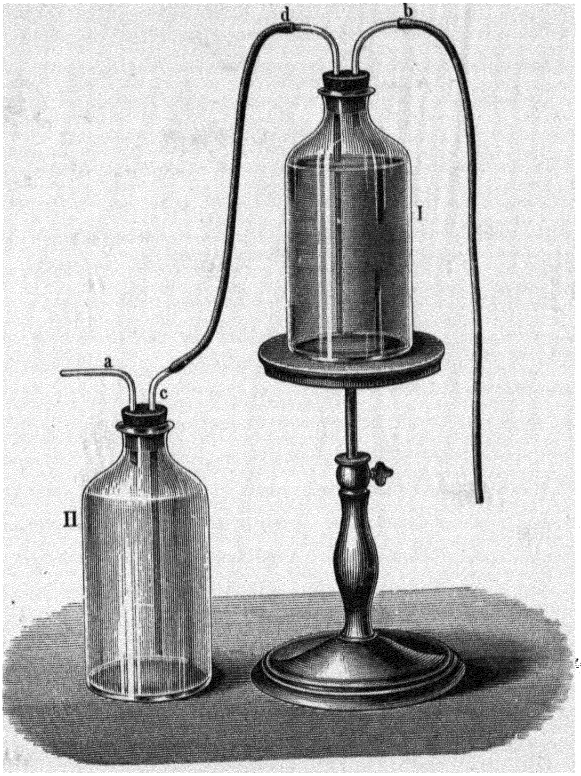

FIG. 149.

When the contents of I. have run out, the rubber tube is detached from *b*, the position of the bottles is reversed so that II. now stands higher, and the rubber tube is attached to *a*. The connection between *c* and *d* is not touched. Usually the siphon begins to act again of its own accord ; otherwise it is started by sucking for a moment at *b*. The quantity of water running out of the top bottle at each turn is noted.

This method has the drawback of requiring an attendant to change the position of the bottles, and is therefore not con-

venient for continuous testing. For this purpose, if a meter is to be dispensed with, a vessel of large capacity, say several cubic feet, should be provided, sufficient to serve for twenty-four hours without special attendance. This vessel can be made of glass, stoneware, or wood lined with lead. It should be provided with a gauge for measuring the height of the water. In order to act uniformly, it should be on the principle of a Mariotte bottle, as described on p. 709, Lunge's fourth edition.

An apparatus has been described by W. S. Strype [1] and an abridged description is given in Lunge's fourth edition, p. 975 *et seq.*

Whatever system is used for aspirating the gases, they must be passed through certain *solutions to absorb the acids* as completely as possible. The different acid compounds of sulphur are estimated together, as are those of nitrogen, whatever degree of oxidation they may possess. The following formulæ agree in the main with those worked out by Hurter and published *by the British Alkali Makers' Association* in 1878.[2] A continuous test over twenty-four hours is taken of the gases escaping from the exit-pipes of the Gay-Lussac towers, aspirating at least 1 cub. ft. per hour by means of any aspirator acting at a constant rate, and recording the volume of gas (V) by means of gauging the aspirator or by a gas-meter. The volume V is reduced to 0° C. and 760 mm. pressure (32° F. and 29·92 in.) by the tables contained in Lunge's *Handbook*, p. 38 *et seq.*,[3] and is now called V'. In order to allow of comparison, the number of cubic feet of chamber-space per pound of sulphur burnt and passed into the chambers is recorded. In this estimate, towers are excluded, but tunnels are included, and the amount of sulphur is taken from the weekly average.

The distance of the testing-hole from the point at which the gases leave the Gay-Lussac towers is also stated. The

[1] *Trans. Newc. Chem. Soc.*, 1880, 55, 367.

[2] These formulæ, with a few improvements in analytical details, are also given in Lunge's *Technical Chemists' Handbook*, 1910, p. 118 *et seq.*

[3] The law requires the cubic foot to be measured at 60° F. and 30 in., which necessitates the use of tables or factors other than those mentioned in the text, but the difference is hardly perceptible, and is within the limits of experimental error.

absorption-apparatus consists of four bottles or tubes (Fig. 150),[1] each containing not less than 100 c.c. of absorbing-liquid, having a depth of at least 3 in. in each bottle. The aperture of inlet tubes must not exceed $\frac{1}{50}$ in. in diameter, this aperture being measured by a standard wire. The first three bottles each contain 100 c.c. of normal caustic-soda solution (40 grams per litre); the fourth, 100 c.c. of distilled water. The caustic soda must be free from nitrogen acids. The gases are tested (1) for total acidity, which is stated in grains of SO_3 per cubic foot of gas, or else in grams per cubic metre; (2) sulphur acids; (3) nitrogen acids—both stated in grains of S and N per cubic foot (or grams per cubic metre). The analysis is carried out as follows:—The contents of the four bottles are combined, taking care not to unnecessarily augment the bulk of the liquid, which is divided into three equal parts, one of which is reserved in case of accidents, etc. The first part is titrated with normal sulphuric acid (49 grams H_2SO_4 per litre), to ascertain total acidity. The number of cubic centimetres of acid necessary for neutralisation is called *x*. The second part of the liquid is gradually poured into a warm solution of potassium permanganate, which is strongly acidified with pure sulphuric acid. A small excess of permanganate must be present, and this must afterwards be reduced by the addition of a few drops of sulphurous-acid solution, until only a faint red tint is visible. Now all nitrogen acids are present as HNO_3, and there is no excess of SO_2. The HNO_3 is estimated by its action on $FeSO_4$. Twenty-five c.c. of a

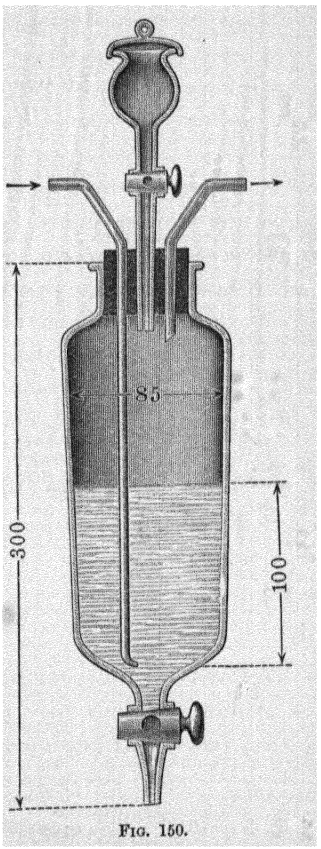

FIG. 150.

[1] Taken from Jurisch, *Schwefelsäurefabrikation*, p. 224.

solution, containing 100 grams of crystallised ferrous sulphate and 100 grams pure sulphuric acid per litre, are put into a flask, 20 to 25 c.c. pure concentrated sulphuric acid is added, the mixture is allowed to cool, and the other mixture, previously treated with permanganate, etc., is added. The flask is closed by a cork fitted with glass tubes. A continuous current of CO_2 is passed through and issues beneath the surface of some water, in order to prevent entrance of air. First, all the air is expelled; then the solutions are introduced, and the contents of the flask are heated to boiling, till the dark colour produced by the formation of NO has changed to a clear light yellow. This takes from a quarter of an hour to one hour, according to the quantity of HNO_3 present and to the amount of the sulphuric acid added. The unoxidised ferrous sulphate is titrated by a semi-normal permanganate solution (yielding 0·004 gram oxygen per c.c.); the amount used equals y. Since the titre of the iron solution changes fairly quickly, it should be tested daily by taking out 25 c.c. with the same pipette used for the operation described above, and ascertaining the amount of permanganate required for oxidising it, say, z c.c. The magnitudes sought are found by the following equations:—

1. *Total Acidity* in grams per cubic metre:

$$SO_3 = \frac{0{\cdot}120(100 - x)}{V'}.$$

1. *Total Acidity* in grains per cubic foot:

$$SO_3 = \frac{1{\cdot}852(100 - x)}{V'}.$$

2. *Sulphur* in grams per cubic metre:

$$S = \frac{0{\cdot}008(600 - 6x - z + y)}{V'}.$$

2. *Sulphur* in grains per cubic foot:

$$S = \frac{0{\cdot}12346(600 - 6x - z + y)}{V'}.$$

3. *Nitrogen* in grams per cubic metre:

$$N = \frac{0{\cdot}007(z - y)}{V'}.$$

3. *Nitrogen* in grains per cubic foot:

$$N = \frac{0{\cdot}10803(z - y)}{V'}.$$

If the nitrogen acids are not to be separately estimated (and the Alkali Act does not require this to be done), the above formulæ can be much simplified. It is only necessary to employ the apparatus shown on p. 476 of Vol. I, Fig. 67,

intended for testing the burner-gases for sulphur acids, or else one of the absorbing-apparatus to be mentioned below. The apparatus is charged with 100 c.c. of normal caustic-soda solution, coloured with phenolphthalein, which acts equally upon SO_2 and H_2SO_4, and this is re-titrated with standard acid. The caustic-soda solution should be as free as possible from carbonate, as CO_2 also acts upon phenolphthalein. The formula for calculation is then No. 1 divided by 3, that is :—

$$SO_3 = \frac{0{\cdot}040(100 - x)}{V'} \text{ grams per cubic metre,}$$

$$= \frac{0{\cdot}617(100 - x)}{V'} \text{ grains per cubic foot.}$$

When the object of testing the exit-gases is merely to ascertain the total acidity, in view of the requirements of the law (p. 482 of Vol. I), it is sufficient to pass a certain volume of the gas through a solution of hydrogen peroxide, which oxidises the SO_2 to H_2SO_4, and then to titrate the acid with caustic-soda solution, using methyl-orange, and calculate to SO_3. In a very exhaustive paper[1] R. F. Carpenter and Linder prove that the best way of proceeding is to employ a mixture of 1 vol. semi-normal caustic-soda solution and 10 vols. hydrogen peroxide solution for the absorption, and afterwards re-titrate, using phenolphthalein at a boiling heat, or methyl-orange in the cold. In this case, the nitrogen acids proper are also absorbed, but NO is only very slightly acted upon. They believe that certain sulphazotised bodies, present in chamber escape gases, are thus also dealt with. They assume that the nitrous smell, sometimes observed in the gases discharged from the bellows aspirator, is caused by the reaction :

$$H_2O_2 + 4HNO_2 = 2HNO_3 + 2NO + 2H_2O.$$

H. J. Watson[2] confirms generally Carpenter's and Linder's results and conclusions, especially the necessity of employing both alkali and hydrogen peroxide. He suggests using five absorbing-vessels, the first two being charged with hydrogen peroxide and the other three with alkaline hydrogen peroxide. The first two show the acidity of the gases, the last three the nitre lost.

[1] *J. Soc. Chem Ind.*, 1902, p. 1490. [2] *Ibid.*, 1903, p. 1279.

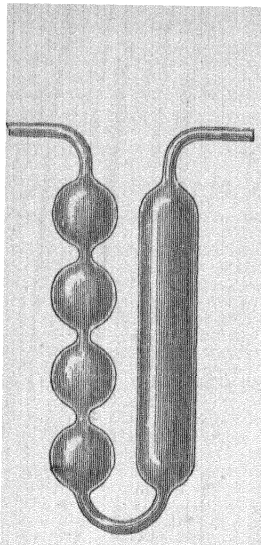

FIG. 151.

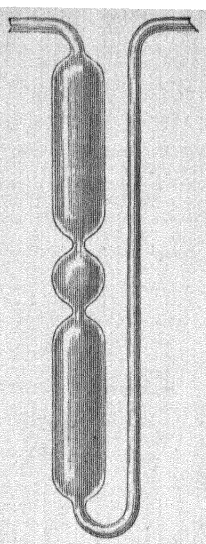

FIG. 152.

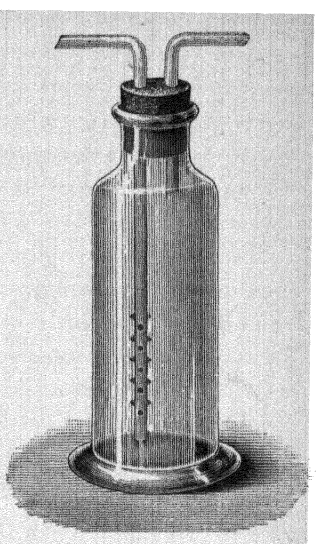

FIG. 153.

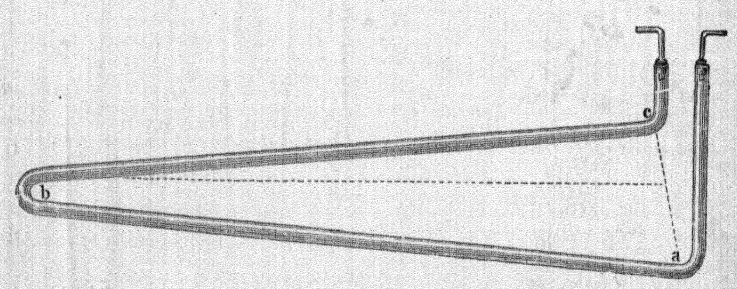

FIG. 154.

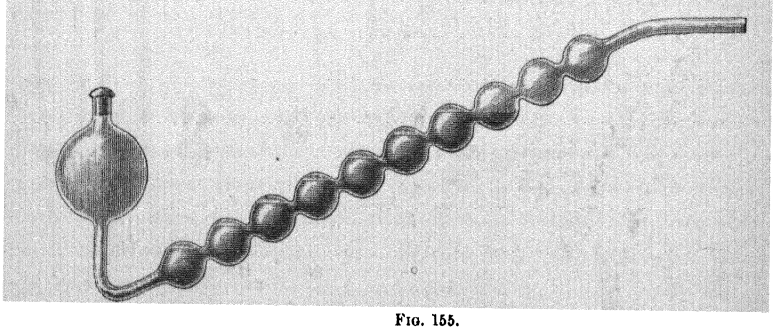

FIG. 155.

The *shape of the absorbing-vessels* is important. When employing ordinary bottles with simple glass tubes dipping below the liquid, the absorption is often incomplete, even if several bottles are used in succession, an arrangement which causes considerable pressure. The use of very narrow inlet-tubes, as described in the *Alkali Makers' Instructions* (see above, p. 300), lessens, but does not entirely avoid, the evil of incomplete absorption. The potash-bulbs used in organic analysis cannot be employed, because it is difficult to empty their contents without loss.

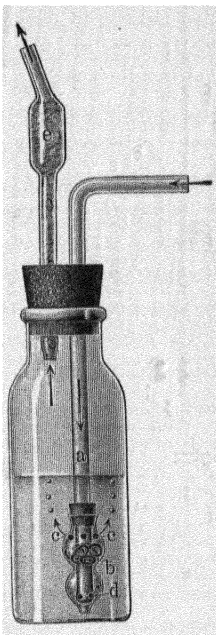

FIG. 156.

The absorption is better when using Mitscherlich's tubes (Fig. 151), of which Todd's tubes (Fig. 152) are but a slight modification. The type of absorbing-bottle shown in Fig. 153 also serves very well. The Pettenkofer tube as modified by Lunge (Fig. 154) is extremely efficient, and a 10- or 15-bulb-tube, as shown in Fig. 155, is still better; one of this type generally suffices for complete absorption.

Ordinary absorbing-bottles fail to act where white mists of acid have to be dealt with, as in the case of the gases from overhead-fired pans or beaker-apparatus for rectified vitriol. In these cases the bottles may be shaken a hundred times or more without entirely removing the white mist. The Alkali Inspectors have, however, elaborated a bottle which performs this service most efficiently. It is shown in Fig. 156, where it will be observed that the absorbing-bulb contains a number of india-rubber rings (cut from ordinary small tubing). The gases pass through the central tube *a*, by small holes *d* near its closed end, into the bulb *b*, and before they issue through the holes *c c* they are broken up into small bubbles by the india-rubber dippings. These are washed by the movement of the liquid in the apparatus, and thus produce a thorough scrubbing of the gas. The upper bulb is $\frac{3}{4}$-in. wide, the lower $\frac{5}{8}$ in., and the bottom-opening $\frac{1}{4}$ in.; these proportions should be

observed in order to attain the object. Exit-tube *e* is filled with glass-wool.

Nitric oxide may be (and generally is) present in the gases after they have passed through the absorbing-bottles, as its oxidation to NO_2, when it is greatly diluted, is an extremely slow process.[1] It can be estimated in an absorbing-tube (Fig. 154), or in a bulb-tube (Fig. 155), interposed between the aspirator and the tubes of the apparatus used for estimating the acids. The bulb-tube is charged with 30 c.c. of semi-normal permanganate solution and several c.c. of sulphuric acid. The gas is passed through for twenty-four hours, and the tube emptied and washed out. Fifty c.c. of ferrous sulphate solution, corresponding to $2z$ permanganate, are then added, and the decolorised liquid re-titrated with permanganate. (If a precipitate of manganese peroxide has been formed in the absorbing-tubes, the tubes should be rinsed with some of the iron solution.) The quantity of the permanganate required after addition of ferrous sulphate is called u. The NO has altogether consumed $(30 + u - 2z)$ c.c. of permanganate, giving :—

In grams of nitrogen per cubic metre of the volume V'.

$$N = \frac{0{\cdot}007(30 + u - 2z)}{3V'}$$

In grains of nitrogen per cubic foot.

$$N = \frac{0{\cdot}10803(30 + u - 2z)}{3V'}$$

The quantity of nitric oxide present in chamber exit-gases may at times be rather considerable without attracting notice, as it oxidises only very slowly when greatly diluted with inert gases. This makes some of the proposed absorbents, such as hydrogen peroxide or a mixture of strong sulphuric and nitric acid, practically useless for the estimation of NO, as proved by Lunge by many laboratory experiments. The paper of Carpenter and Linder, quoted p. 303, corroborates this. For this reason Lunge first proposed in 1881 the use of an acid solution of potassium permanganate in the apparatus described here. Even this process requires a very good absorbing-apparatus and a very slow stream in order to take all the NO out of the gases.

According to Divers,[2] the absorption of NO is very easily effected by a concentrated alkaline solution of sulphites, for example, 40 grams Na_2SO_3 and 4 grams KOH, dissolved in 200 c.c. water.

[1] *Cf. 40th Alkali Report*, p. 27. [2] *J. Soc. Chem. Ind.*, 1902, p. 1492.

Baudisch and Klinger[1] pass the gas, in which nitric oxide is to be estimated, into a moistened pipette containing some damp caustic potash, and allow some air to enter. The NO at once combines with the O to form N_2O_3, which is immediately absorbed by the KOH, no N_2O_4 being formed. By measuring the air before and after the experiment, the quantity of NO is ascertained, as four-fifths of the contraction observed corresponds to the NO absorbed, and one-fifth to the oxygen consumed in its oxidation: $4NO + O_2 = 2N_2O_3$. At the end of the experiment there must still be some free oxygen in the pipette.

Nitrous oxide, N_2O, occurs in small quantities in the exit-gases from the Gay-Lussac tower, and has been estimated in these by Inglis, as mentioned on p. 287, where the analytical methods used by him are described. Other methods for the estimation of N_2O are described on p. 484, Vol. I. Its estimation in presence of NO is described by Moser,[2] who absorbs the NO by potassium permanganate, or adds to the gases hydrogen peroxide, and titrates the nitric acid formed; by Knorre and Arndt;[3] and by Pollak.[4]

Oxygen.—Pérégrin[5] describes a registering apparatus for the estimation of oxygen. The gas flows into a wooden chamber of about 30 litres capacity. A light rubber balloon of 10 litres capacity, filled with hydrogen and suitably varnished to prevent diffusion, is suspended in the chamber by means of a fine wire attached to one arm of a pivoted beam, and any rise or fall of the balloon due to changes in the density of the gas in the chamber is recorded by the other, and longer, arm of the beam, on a drum which rotates once in twenty-four hours.

The gas collecting in the aspirating-vessel of any of the apparatus described above, being an average sample of the exit-gases free from acids, is very conveniently employed, in preference to samples taken at random over the day, for *estimating the oxygen* contained in the exit-air. This estimation has been previously described (p. 481 of Vol. I), and it is only necessary to show here how the estimation of oxygen in the exit-gas may be used for *ascertaining the quantity of sulphur burnt*, the result being expressed in grams per litre of the exit-gas, so that the

[1] *Ber.*, 1912, p. 3231. [2] *Z. anal. Chem.*, 1911, p. 401.
[3] *Ber.*, 1909, p. 2136. [4] Treadwell, *Quant. Anal.*, 4th ed., p. 597.
[5] *J. Soc. Chem. Ind.*, 1916, p. 1216.

quantity of sulphur lost in that gas may be put in direct comparison with the total sulphur used. For this the following formula has been proposed by Lunge in *Dingl. polyt. J.*, **226**, 634 :—

$$(20{\cdot}95 - a) \times 0{\cdot}009637 \times \frac{1}{1{\cdot}00367\, t} \times \frac{h}{760} = x.$$

Here a denotes the percentage of oxygen in the exit-gas, t its temperature, h the barometric pressure in millimetres, x the total quantity of the sulphur actually burnt, expressed in grams per litre of the exit-gas. The quantity actually found should be compared with this in order to find the percentage of loss. It should not be overlooked that no account is here taken of the sulphur remaining in the cinders.

Theory of the Formation of Sulphuric Acid by the Chamber-process.

When describing in previous chapters the behaviour of sulphur dioxide towards the various nitrogen compounds in presence of water, sulphuric acid, etc., and the formation and decomposition of nitrososulphuric acid, it has been necessary to forestall theoretical considerations repeatedly, but these will now be brought forward connectedly and in detail.

From the commencement, the fact must be borne in mind that during the burning of sulphur, whether in the form of brimstone, pyrites, or blende, etc., sulphur dioxide (SO_2) is the chief product. The formation of sulphuric anhydride or acid, always occurring at the same time, is not taken into account here, as it is merely a secondary reaction, and still leaves it necessary to explain the oxidation of the sulphur dioxide in the lead-chambers. That this does not take place to an appreciable extent by the direct action of the atmospheric oxygen, may be taken as established. But it is just as certain that the oxygen of the nitre introduced into the process does not suffice to account for it; for the sulphur dioxide from 100 parts of sulphur requires another 50 parts of oxygen in order to be oxidised to sulphuric acid, which amount would correspond to 88·5 parts of nitrate of soda even if this compound were reduced to nitrogen. It is well known that, under

favourable conditions, only $\frac{1}{30}$ of the above quantity of nitre is used, and this fact must now be explained.

The history of the various theories of the chamber-process is fully dealt with in Lunge's fourth edition, p. 987 *et seq.*, but only the salient features of the various investigations, so ably and fully dealt with by Lunge, will be abstracted here. The first theory was propounded as early as 1806 by Clément and Désormes.[1] The presence of water they explained as necessary, first, for keeping the temperature of the reaction sufficiently low, and secondly, for condensing the sulphuric acid as it forms. They observed in the process the production of white star-shaped crystals, which on contact with water gave out nitre-gas with a strong evolution of heat, and they suspected that this compound played a prominent part in the acid-forming process.

H. Davy showed, in 1812, that the presence of water is absolutely necessary,[2] because in the dry state the gases do not react upon each other. A small quantity of water, however, added to the mixture of sulphur dioxide and nitrous vapours causes the formation of the crystals observed by Clément and Désormes. Davy, therefore, considered that body an intermediate link indispensable for the formation of sulphuric acid as expressed by the following :—

$$\text{I. } 2SO_2 + 3NO_2 + H_2O = 2SO_2(OH)(ONO) + NO;$$
$$\text{II. } 2SO_2(OH)(ONO) + H_2O = 2SO_2(OH)_2 + NO_2 + NO;$$
$$\text{III. } 2NO + 2O = 2NO_2.$$

An *apparently* simpler explanation of the vitriol-chamber process was given by Berzelius.[3] He did not regard the formation of chamber-crystals as a necessary intermediate process, but only as an exceptional case happening in some parts of the chamber where moisture is wanting. The process, according to him, is the transference of oxygen from "nitrous acid" to sulphur dioxide (and water), producing sulphuric acid and nitric oxide, from which, by means of oxygen, nitrous acid is regenerated according to the following :—

$$(1)\ SO_2 + N_2O_3 + H_2O = H_2SO_4 + 2NO;$$
$$(2)\ 2NO + O = N_2O_3.$$

[1] *Ann. Chim.*, 59, 329. [2] Berzelius, *Lehrbuch*, 1, 471.
[3] *Lehrbuch der Chemie*, Woehler's translation, 4th ed., 1835, 2, 12.

But Lunge has shown (*Ber.*, 1888, p. 3225) that Berzelius, as was natural in those days, made no sharp distinction between N_2O_3 and N_2O_4, and evidently by "nitrous acid" often meant N_2O_4. The following equations were later held to express the vitriol-chamber process :—

$$(3)\ SO_2 + NO_2 + H_2O = H_2SO_4 + NO\ ;$$
$$(4)\ NO + O = NO_2.*$$

* Here, as in all other instances, the symbols N_2O_4 and NO_2 will be used as interchangeable according to convenience of expression.

Another theory, that of Peligot, published in 1844,[1] was accepted, more especially in France, for a long time; even Kolb[2] adhered to it, as did also Pelouze and Frémy.[3]

Peligot, like Berzelius, denied that the chamber-crystals had an essential share in the formation of sulphuric acid, or that they appeared at all in the regular process, either in a solid form or in solution. He attributes the oxidation of the sulphur dioxide within the lead-chamber exclusively to nitric acid, not to the lower oxides of nitrogen :—

$$\text{I.}\ SO_2 + 2NO_2 \cdot OH = SO_2(OH)_2 + N_2O_4\ ;$$
$$\text{II.}\ 2N_2O_4 + H_2O = N_2O_3 + 2NO_2 \cdot OH\ ;$$
$$\text{III.}\ 3N_2O_3 + H_2O = 4NO + 2NO_2 \cdot OH\ ;$$
$$\text{IV.}\ 2NO + 2O = N_2O_4.$$

The researches of R. Weber in 1866 and 1867[4] proved the complete futility, in all respects, of Peligot's theory, and greatly contributed towards elucidating the process within the lead-chamber.[5]

He showed that dilute nitric acid has very little effect on sulphur dioxide at ordinary temperatures, but the same acid, with nitrogen peroxide vapour dissolved in it, has a very vigorous action.

This proves that the nitrous acid generated by the contact of nitrogen peroxide and water oxidises the sulphur dioxide much more readily than nitric acid does. Therefore nitrous

[1] *Ann. Chim. Phys.* (3), **12**, 263.

[2] *Études sur la fabrication de l'acide sulfurique*, Lille, 1865, p. 22.

[3] *Traité de chimie*, second ed., **1**, 398.

[4] Poggendorff's *Annalen*, **127**, 543, and **130**, 329.

[5] Some parts of Weber's as well as of Winkler's work have been noticed in Vol. I, p. 257 *et seq.*

acid is undoubtedly the primary cause of the reaction for the formation of sulphuric acid when moist air meets sulphur dioxide and the vapour of nitrogen peroxide. The nitric acid which is formed on the decomposition of N_2O_4 by water remains undecomposed by SO_2 *if much water is present.* Under certain circumstances, however, as will be shown below, the nitric acid is also decomposed.

For the chamber-process the behaviour of N_2O_4 and N_2O_3 towards sulphuric acid of various degrees of dilution with water must also be taken into account, as those gases come into contact with the acids, both in the form of minute drops suspended in the atmosphere of the chamber and in the stock collected at the bottom. According to their degree of dilution the sulphuric acids contain nitrososulphuric acid (chamber-crystals), free N_2O_4, or N_2O_3, as has been explained in detail on p. 253 *et seq.* of Vol. I; but all these solutions, when their density is much higher than that of ordinary chamber-acid, are rapidly decomposed by sulphur dioxide, sulphuric acid being formed. The decomposition of the absorbed vapours, by means of water for the purpose of forming nitric acid, is therefore quite improbable; but the water is necessary for forming the hydrate SO_4H_2, and therefore only in its presence can SO_2 be promptly oxidised by N_2O_3.

It is of importance, in practice, that moderately concentrated mixtures containing nitric acid are more easily decomposed by sulphur dioxide than highly concentrated ones. When nitrous acid is dissolved in the pure hydrate SO_4H_2, or even in ordinary vitriol of 168° Tw., sulphur dioxide does not act upon it at all, or at least very incompletely.

According to Weber's theory, the following process takes place within the chambers:—The sulphur dioxide is oxidised, mainly by the oxygen of the nitrous acid, which thereby passes into nitric oxide. This occurs, however, only when the nitrous acid is dissolved in water or in dilute sulphuric acid, this solution being formed either direct from free N_2O_3 or by the decomposition of N_2O_4. In the latter case nitric acid is formed at the same time. This can only be decomposed by the mediation of already-formed sulphuric acid. The part played by the water has just been explained.

There is an agreement in many, but not in all, points

between the opinions of Weber and those published almost simultaneously by Cl. Winkler.[1]

The fact that Weber points chiefly to N_2O_3, Winkler principally to N_2O_4, as the active agents in the chamber-process, does not form a very essential difference in their views, as neither of them assumes either of these oxides to be formed exclusively. A more fundamental difference is that Weber, like Berzelius, does not admit the intermediate formation of nitrososulphuric acid as an essential feature of the process, whilst Winkler does, thus reverting to Davy's theory, which he merely develops in the light of modern knowledge, and more especially of his own investigations.

When, in 1878, the first edition of Lunge was written, the question had not practically advanced beyond the labours of Weber and Winkler, both of whom relied on laboratory experiments, not on researches made with actually working vitriol-chambers.

A solid basis for a true theory of the vitriol-chamber process could only be formed by investigating the manufacturing process itself in all its stages, and, both as regards normal and irregular work, by an extended series of gas-analyses and other pertinent observations. The first complete investigation of this kind was that made by Lunge in conjunction with Naef at the Uetikon works, near Zurich, to which allusion has already been made.[2] The results of this investigation have not been shaken by any others carried out since, so far as the facts of the case are concerned; but the explanations at that time given by Lunge and by other chemists have had to be modified considerably, especially in consequence of the further experimental work conducted by Lunge in 1885.[3] He proved that in the dry state, and out of contact with sulphuric acid, nitric oxide combines with oxygen present in excess to form nitrogen *peroxide* almost exclusively. If dry nitric oxide, being in excess, meets with an insufficient quantity of oxygen, a considerable amount of N_2O_3 is formed together with N_2O_4 (according to the view held at that time). In the presence of moisture, nitric

[1] *Untersuchungen, etc.*, p. 20.

[2] *Chem. Ind.* 1884, pp. 5 to 19.

[3] *J. Chem. Soc.*, 47, 465; *Ber.*, 18, 1384; *cf.* other work done before and after, mentioned in Vol. I, p. 258 *et seq.*

oxide and excess of oxygen combine to form nothing but nitric acid. *Dilute* sulphuric acid (sp. gr. 1·405) acts on the whole like water, but a small quantity of nitrous acid is formed, as much as can exist in a stable solution in the acid (nitroso-sulphuric acid cannot exist in acid of this concentration). Perhaps the most important observation, combined with others formerly made, was this :—If *strong* sulphuric acid is in presence of a large excess of oxygen, and nitric oxide is slowly passed into it, only that portion of the NO which is in *immediate* contact with sulphuric acid, and which therefore forms nitroso-sulphuric acid, is not oxidised beyond the state of N_2O_3 (as previously found by Winkler and Lunge) ; but all the gaseous molecules coming into contact with oxygen *outside* the acid, even immediately above it, behave like dry NO and excess of O generally—that is, they combine to form N_2O_4.

This last observation made it impossible to maintain, as had been done in the first edition of Lunge and in some of his later papers, that the reason why the excess of O within the vitriol-chambers produces N_2O_3 from the NO instead of NO_2 (or rather a gaseous mixture of approximately that composition) lies in the fact that there is a mist of sulphuric acid throughout the chamber ; for the liquid particles of sulphuric acid forming the mist are still at very great distances from one another relatively to the amount of NO and O present, and wherever these gases act upon one another otherwise than in immediate absolute contact with the acid, they will yield not N_2O_3, but N_2O_4.

Raschig [1] asserted that nitric oxide, even in presence of a very large excess of oxygen, is not converted into N_2O_4, but into N_2O_3, provided that the oxygen is diluted with nitrogen, as in atmospheric air. This assertion, however, which was even at that time opposed to the statements of all other chemists, was entirely disproved by Lunge's researches,[2] which showed that Raschig's experiments were badly conducted, and that NO is transformed into nitrogen peroxide by atmospheric air just as by pure oxygen.

The whole of Raschig's arguments and hypotheses are vitiated by the recognition of the fact that nitrogen trioxide, N_2O_3, does not exist in the gaseous form except in traces.

[1] *Annalen*, 248, 135. [2] *Berl. Ber.*, 1888, p. 3234.

Of course, Lunge's theory is also affected by this fact, but, as shown on p. 253 of Vol. I, is altogether compatible with the light gained by more recent knowledge, since a mixture of $NO + NO_2$ behaves towards sulphuric acid exactly like N_2O_3.

Raschig's own theory of the vitriol-chamber process,[1] propounded at that time, assumed as an intermediate stage the temporary formation of a compound which he calls "dihydroxylamine-sulphuric acid," having the formula $(OH)_2NSO_2OH$, a compound which nobody has seen, and the preparation of which, in the free state, he himself did not expect to be possible. He assumes that this compound is formed when nitrous and sulphurous acid meet, but is instantly decomposed with more nitrous acid into NO, SO_4H_2, and H_2O; NO is then again oxidised to nitrous acid, and the process begins anew.

Lunge has shown[2] how unfounded are all the arguments adduced by Raschig for his view. A summary of the controversy was given by Hamburger in *J. Soc. Chem. Ind.*, 1889, p. 164.

Several facts have to be reconciled in any true theory of the lead-chamber process: first, the fact that the chambers contain at first a mixture of more than 1 mol. NO to 1 mol. NO_2, later on almost an exactly equal number of molecules of NO and NO_2, but in regular work never any excess of NO_2 over this proportion; an excess of NO_2, which may occur in irregular working, has in former discussions been called "free" nitrogen peroxide (Lunge and Naef's observations at Uetikon); second, that NO and an excess of O combine to form N_2O_4, and it is only where NO and O meet, at the same time, sulphuric acid of sufficient concentration that they form nitrous acid, not in the free state, but as $SO_2(OH)(ONO)$; NO and O, in the presence of H_2O and SO_2, may also form directly $SO_2(OH)(ONO)$. A new theory of the chamber-process, based on these fundamental and all other observed facts, had been clearly, although very briefly, indicated by Lunge in his paper of 1885,[3] and it was further developed in subsequent papers, especially *Ber.*, 1888, pp. 67 and 3323.

[1] *Annalen*, **241**, 242.
[2] *Ber.*, 1888, pp. 67 and 3223.
[3] *J. Chem. Soc.*, **47**, 470.

The principal ideas of the theory were stated by him in 1885,[1] as follows:—"*Sulphur dioxide combines directly with nitrogen trioxide, oxygen, and a little water to form nitrososulphuric acid, which floats in the chamber as a mist; on meeting an excess of water, also floating about as a mist* [probably mostly or all in the form of very dilute sulphuric acid], *the nitrososulphuric acid splits up into sulphuric acid, which sinks to the bottom, and nitrogen trioxide, which begins to act anew. Hence it is not, as hitherto generally assumed, the nitric oxide,* NO, *but the nitrogen trioxide,* N_2O_3, *which acts as carrier of oxygen in the vitriol-chamber process.*" The formation of sulphuric acid is not brought about by alternate *oxidation* of NO to N_2O_3 or N_2O_4, and subsequent *reduction* of these compounds to NO, but by a *condensation* of nitrous acid with sulphur dioxide and oxygen into nitrososulphuric acid, and a subsequent splitting up of this compound by an excess of water, as represented by the following equations:—

(1) $SO_2 + NOOH + O = SO_2(OH)(ONO)$
(2) $SO_2(OH)(ONO) + H_2O = H_2SO_4 + NOOH.$

At the same time, he pointed out that these reactions were or might be locally modified by special circumstances in different parts of the chamber, and this matter was treated in detail in his papers of 1888.

It is seen at once that this theory goes back to Davy's theory of 1812, subsequently upheld, among others, by L. Gmelin and Cl. Winkler, according to which the intermediate formation of nitrososulphuric acid (chamber-crystals) is a necessary intermediate stage in the chamber-process. But Lunge's new theory removed the complication of those former views, and their partial contradictions to observed facts, by denying the necessity of a reduction to NO as an indispensable factor in the process, because from this reduction the formation of an excess of nitrogen peroxide in the chamber would follow.[1] This new theory is considered in detail below, and also the modifications which the process suffers by local circumstances in certain parts of the chamber.

It should be remembered that the gases of a normally

[1] By "free" nitrogen peroxide is meant any excess of NO_2 over the proportion required to form N_2O_3 with NO, here as well as in all other places.

working chamber contain at first an excess of NO, further on and right to the end, only an equimolecular mixture of $NO + NO_2$, equivalent to N_2O_3. An excess of nitrogen peroxide over that proportion is found only in case of irregular work, when an unnecessary excess of nitrous gases is sent into the chambers, the formation of sulphuric acid is finished too early, and the last part of each chamber contains extremely little SO_2; in this case only free NO_2 is found there. A greater or smaller excess of oxygen is without influence on the question of whether $NO + NO_2$ is formed, or more NO_2.

Although N_2O_3, when liberated from its combination with sulphuric acid, immediately dissociates for the most part into $NO + NO_2$, a very small quantity of N_2O_3 remains as such and can enter into the above-stated reaction (1) (p. 315); and according to the law of mass-action more $NO + NO_2$ immediately recombine to form N_2O_3, so that no sensible quantity of NO has time to form, with oxygen, "free" nitrogen peroxide, as SO_2 is present everywhere and leads to the formation of SO_5NH.

The same compound will be formed by SO_2 from any locally existing free NO_2, according to equation (9) (see p. 318).

The orange vapours filling the chambers consist of a mixture of NO and NO_2, the former being in excess in the light-coloured front part of the chamber-system, whilst later on the proportion (as shown by analysis) is almost exactly equal to $NO + NO_2$, which constantly acts again with H_2O, SO_2, and O to form SO_5NH, and is re-formed from the latter by the action of more H_2O, as shown by the equations :—

$$(1\,b)\ SO_2 + NOOH + O = SO_5NH,$$
$$(2\,b)\ 2SO_5NH + H_2O = 2H_2SO_4 + N_2O_3,$$
$$(3\,b)\ N_2O_3 + H_2O = 2NOOH;$$

or else :—

$$(1\,c)\ 2SO_2 + NO + NO_2 + O_2 + H_2O = 2SO_5NH,$$
$$(2\,c)\ 2SO_5NH + H_2O = 2H_2SO_4 + NO + NO_2.$$

The reactions formerly assumed by Berzelius (with the qualification expressed on p. 309), R. Weber, Lunge, and, indirectly, by Raschig, namely :—

$$(3)\ SO_2 + N_2O_3 + H_2O = H_2SO_4 + NO,$$
$$(4)\ 2NO + O = N_2O_3,$$

cannot represent the chamber-process: for, in the first place, there would be everywhere in the chambers, up to the end, a large number of molecules of NO together with N_2O_3, which is not the case; and secondly, the reaction (4) does not take place at all except in *immediate* contact with (strong) sulphuric acid, and in that case, no free N_2O_3 is formed, but SO_5NH. The reactions, therefore, are necessarily those represented by equations (1) above or (7) below. If in the back parts of the chambers free NO (more than is required for the equimolecular mixture $NO + NO_2$) existed to any extent for any appreciable length of time, it would there be oxidised to nitrogen peroxide. This in contact with either water or sulphuric acid will form nitric acid, which should be found, at least to a great extent, unchanged, as it is a sufficiently stable compound in that part of the chamber, where there is far too little SO_2 and too low a temperature to reduce much HNO_3. But since HNO_3 is *not* found in normal working back-chambers, nor in the Gay-Lussac acid, *any theory based on the regular reduction of nitrous vapours down to nitric oxide*, NO, *cannot be accepted as true*, as it involves the formation of "free" N_2O_4, and subsequently of HNO_3.

It is important for this theory to notice that sulphuric acid, as found in the chambers, certainly dissolves very sensible quantities of SO_5NH, and indeed all the "drips" and even the bottom acid of the back-chambers testify to this. But this solubility, or, as it is better expressed, the stability, of SO_5NH is greatly diminished both by a higher temperature and by dilution of the acid (*cf.* Vol. I, p. 259 *et seq.*), and this behaviour is indeed the foundation of all former processes for denitrating nitrous vitriol (p. 207 *et seq.*). In the vitriol-chambers the temperature is much above that of the atmosphere, and the second condition is also fulfilled, for as soon as the SO_5NH is formed at any point, and floats about in the form of a fine mist, it meets with particles of water or of dilute sulphuric acid, and it must suffer decomposition according to equation (2), p. 316, so that sulphuric acid and nitrous acid are formed. Only the nitrososulphuric acid which is in immediate contact with the bottom-acid will be dissolved by it, and thus be temporarily withdrawn from decomposition. This takes place to a greater extent in the back chambers,

whilst in the front chamber, where both the higher temperature and the excess of SO_2 act as denitrating agents, the bottom-acid shows little or sometimes even no "nitre."

The views hitherto brought forward do not, however, explain the whole of the vitriol-chamber process. They must be modified for the first part of the chambers, which is filled with opaque white clouds, and which Lunge and Naef have proved to contain much NO in excess above the proportion $NO + NO_2$. The temperature is highest and the formation of acid most active in this region. It is possible that here, the following direct reactions take place :—

$$(5)\ SO_2 + NO_2 + H_2O = H_2SO_4 + NO,$$
$$(6)\ SO_2 + 2NOOH = H_2SO_4 + 2NO,$$

which would explain the occurrence of NO. This, when it meets SO_2 and O, both being present here in large excess, forms nitrososulphuric acid directly :—

$$(7)\ 2SO_2 + 2NO + 3O + H_2O = 2SO_5NH.$$

Locally, where water is in excess, nitric acid will be formed, but in this part of the chamber where the nitric acid is in the state of vapour, and where it at once meets an excess of SO_2, it is instantly reduced by the reaction :—

$$(8)\ SO_2 + HNO_3 = SO_5NH.$$

In fact, in this first part of the chambers the conditions are still altogether analogous to those prevailing in the immediately preceding Glover tower, and are entirely different from those occurring in the back part of the chambers, where the temperature is lower and there is very much less SO_2 present. In the front part the NO finds such an excess of SO_2, O, and H_2O, that the formation of N_2O_4 is either altogether precluded, or if any small quantity of it is locally formed it must be instantly absorbed again, according to equation :—

$$(9)\ 2SO_2 + N_2O_4 + O + H_2O = 2SO_5NH.$$

In the first part of the chamber-system "free" nitrogen peroxide does not and cannot exist in appreciable quantities, and therefore the formation of sulphuric acid according to equation (5) *does not take place to any appreciable extent.* Equation (6) is practically on the same lines.

This does not yet explain why there is a large excess of

NO present in the first part of the chambers. The explanation is found in a secondary reaction which, under the existing conditions, is bound to occur, viz. :—

$$(10)\quad 2SO_5NH + SO_2 + 2H_2O = 3SO_4H_2 + 2NO.$$

This is, of course, precisely similar to the reaction which takes place in the Glover, the conditions being identical in both cases, namely, presence of large quantities of nitroso-sulphuric acid, of SO_2, of H_2O, and an even higher temperature than that near the top of the Glover tower, where the inflowing acid has a cooling action. Thus more NO is formed than can be at once taken up by reaction (7).

The general results arrived at are as follows :—The *principal reactions* leading to the formation of sulphuric acid in the vitriol-chambers are the *formation of nitrososulphuric acid* from sulphur dioxide, oxygen, and nitrous acid (eq. 1), and its subsequent *decomposition* when meeting with water or dilute sulphuric acid (eq. 2). Whether N_2O_3 exists for an appreciable time as undecomposed vapour or not, is not a decisive point in this case, as the hydrate NOOH may be introduced and as the components $NO + NO_2$ act in the same way as N_2O_3. Besides this principal reaction, another set of reactions takes place in the first part of the chambers, where the nitrososulphuric acid is partially denitrated by the excess of sulphur dioxide (eq. 10), and the nitric oxide thus formed combines directly with SO_2, O, and H_2O to re-form SO_5NH (eq. 7). All the other reactions enumerated above either play no part whatever or only an insignificant part in the chamber-process, and "free" nitrogen peroxide especially does not occur at all in normally working chambers.

Nothing is more certain in the manufacture of sulphuric acid than that the process of converting sulphur dioxide into sulphuric acid takes place in a regular way only by the action of a large excess of oxygen and of nitrous vapours; in the case of a smaller excess of these agents sulphur dioxide escapes into the air. Both theory and practice show that even with the greatest excess of oxygen it is not possible to effect an absolutely complete oxidation of SO_2. It is generally agreed that the best practical limit is attained if the exit-gases contain, in the form of SO_2, 0·5 per cent. of the sulphur originally

employed. The rate at which the formation of sulphuric acid takes place under the given conditions of a certain excess of oxygen and of nitrous vapours has been observed experimentally, and has been mentioned before (p. 292 *et seq.*). It has also been mathematically deduced, first by Hurter,[1] afterwards by Sorel;[2] but their very hypothetical calculations lay claim to interest mostly on the ground that they are in general accordance with previously observed facts.[3] Both authors also represent the normal working of the chambers by curves, with which Hurter compares the practical results of Mactear, and Sorel those of Lunge and Naef (which were not published at the time of Hurter's theoretical research).

Lunge in his fourth edition, p. 964, compared Hurter's curves with his own and Naef's conclusions. The following diagram is given, in which Sorel represents the process (Fig. 157) both by his theoretical curves (drawn in full lines)—the upper one representing a loss of 0·5, the lower a loss of 24 per cent. of sulphur—and by the results obtained by Lunge and Naef. Lunge (*ibid.*) pointed out that whilst, on the whole, the rate of formation of the acid is in agreement with the theoretical curves, there are distinct breaks corresponding to the points where the gases leave one chamber to enter the next. The explanation of this phenomenon has been gone into to some extent. Sorel's explanation, although in full agreement with Lunge's theory of the vitriol-chamber process, amplifies it by specifying more distinctly the conditions under which either the first or the second of the main reactions takes place:—

(1) $SO_2 + NOOH + O = SO_5NH$,
(2) $SO_5NH + H_2O = H_2SO_4 + NOOH$.

In an inert atmosphere nitrososulphuric acid will give up more or less N_2O_3, according to the concentration of the sulphuric acid, the quantity of nitrous (or nitrososulphuric) acid,

[1] *J. Soc. Chem. Ind.*, 1882, p. 52.

[2] In his frequently quoted paper.

[3] Sorel (*Fabr. de l'ac. sulf.*, p. 566) maintains that the first proposition of Hurter's is self-evident, but that the remaining propositions are mathematically untenable; moreover, that some of Hurter's conclusions, drawn from his mathematical reasoning, are partly contrary to experience. This is certain, that practice has not profited in any respect whatever from his theory.

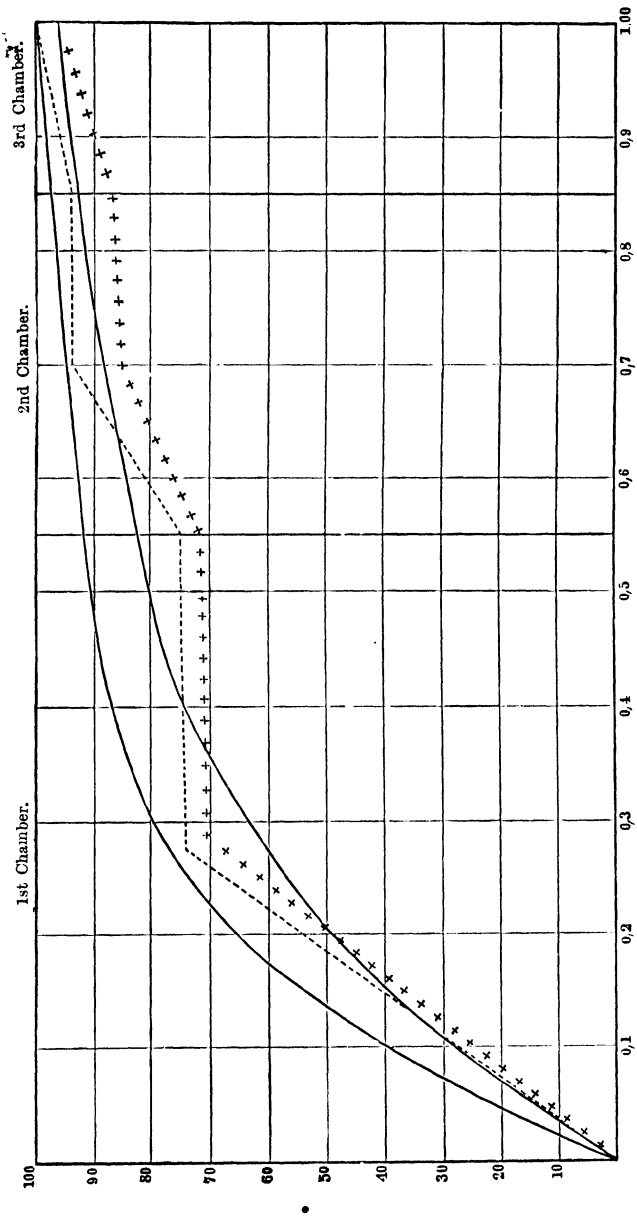
3rd Chamber.
2nd Chamber.
1st Chamber.
100
90
80
70
60
50
40
30
20
10
0,1
0,2
0,3
0,4
0,5
0,6
0,7
0,8
0,9
1,00

FIG. 157.

and the temperature. If a certain quantity of N_2O_3 is removed from the surrounding gases, either directly or by reduction to NO, the acid will yield up more N_2O_3; if, on the other hand, the surrounding atmosphere becomes richer in N_2O_3 by oxidation of NO, the acid will again take up some N_2O_3. The tension of N_2O_3 in its solution in H_2SO_4 is increased by a rise of temperature, but much more by diluting the acid. If, therefore, there exist in an atmosphere containing a certain quantity of N_2O_3, two solutions of N_2O_3 in sulphuric acid, one of them in concentrated, the other in dilute sulphuric acid, the former will enrich itself in N_2O_3 at the expense of the latter, even if it be to a certain extent hotter than the latter. Even the presence of SO_2 does not prevent the solution of N_2O_3 in sufficiently concentrated acid, provided that oxygen is present in excess and that the tension of the N_2O_3 (actually present or capable of formation from NO and O present) is greater than that of the acid in question. On the other hand, the SO_2 will decompose (*i.e.* denitrate) the acid if the outer tension of N_2O_3 is less than that of the acid, if the latter is diluted or if the temperature is raised. [These are indisputable facts, well known before Sorel, but very clearly put by him. In addition he brought in the "tension" of N_2O_3, about which he could not have known very much in detail, and which, in the light of modern theories, would be partly or entirely replaced by the mass-action of the vapours.]

Lunge interprets Sorel's ideas as follows: he assumes that he has a certain definite quantity of acid of 57° Bé. (130°·4 Tw.), containing so much N_2O_3 that for a specified temperature the equilibrium with the surrounding gaseous mixture is established. This acid floats as a mist in the gaseous mass. Suppose a certain volume of this gaseous mass is cooled down, the pressure remaining the same; then part of the aqueous vapour contained in the gaseous mixture will be precipitated in a liquid form and will dilute the acid. The acid will thus become incapable of withdrawing all its N_2O_3 from the influence of the SO_2 present; some NO will be formed, but also some H_2SO_4, by which the acid becomes more concentrated. If now the gaseous mass is brought back to the former, higher, temperature, the acid must, in accordance with the rise of temperature, yield up aqueous vapour, till it

has again attained the density of 57° Bé., at which it once more fixes NO and O as N_2O_3.

Leaving out of consideration the secondary reactions, Sorel, like Lunge, regards the intermediate formation of nitroso-sulphuric acid (the fixation of oxygen upon sulphur dioxide by means of nitrous acid) as one of the principal reactions, followed by the decomposition of that compound, by dilution with water into sulphuric acid and nitrous acid.

The principal cause determining which reaction takes place, is the *temperature*. The temperature near the leaden walls of the chamber is considerably less than that of the inner parts; therefore the gases must assume a quick rotation round a nearly horizontal axis, and each minute drop of acid, according to the change of vapour-tensions, must first be concentrated in the central portion and then be diluted again near the walls. Take, for example, a chamber-acid of 116° Tw. or 67 per cent. H_2SO_4. If, as was the case in a special experiment, the temperature next to the walls is 75°, that in the centre 90°, the vapour-tension of 67 per cent. acid next to the wall will be 27 mm. (*cf.* the table, Vol. I, p. 215); and since the acid floating in the centre must have the same vapour-tension, but the higher temperature of 90°, its concentration (according to the same table) must be 73 per cent. H_2SO_4 or 130°·4 Tw. If, for instance, the acid near the wall had contained only 64 per cent. H_2SO_4, its vapour-tension would have been 37·4 mm., and the hotter acid in the centre would at equal tension have contained 71 per cent. or 126° Tw. A number of observations made by Sorel at working-chambers show that these supposed differences do exist, which proves that the assumption of an equal vapour-tension all through the chamber is correct, and consequently also the assumption that generally the concentration of the acid is greater near the centre than near the walls, where the cooling action of the air comes into play. But as the greater concentration of the acid favours the fixation of nitrous vapours by SO_2 and O as SO_5NH, and the greater dilution favours the decomposition of this compound into H_2SO_4 and N_2O_3, it follows that the formation of SO_5NH takes place chiefly in the centre, and that of H_2SO_4 principally near the walls. The neighbourhood of the walls thus increases the production, as the cooling brings about the condensation of

water, the dilution of the nitrous acid, and its decomposition into H_2SO_4 and N_2O_3. To a smaller extent production is also effected by the neighbourhood of the acid layer at the bottom, which is both cooler and more dilute than the acid floating about in the centre. All this is indirectly, but certainly, proved by the fact that a few centimetres from the wall, where the formation of H_2SO_4 must be strongest, and also a little above the bottom acid, the greater intensity of the reactions is manifested by a higher temperature.

As the gaseous current moves nearer the end of the chamber it becomes poorer in SO_2, and the reactions are therefore less intense. Moreover, observation shows that the temperature in the second half of the chamber hardly sinks at all in the centre, and sinks only 2° near the walls. As less H_2SO_4 is made at this point, the acid in the centre is more dilute, and is less able to fix N_2O_3 and SO_2 as SO_5NH. This reaction is also hindered by the smaller quantity of SO_2 present in the gases. This, according to Sorel, explains the almost total cessation of the reactions in the back part of the first chamber, observed by Lunge and Naef; and it also explains the revival of the process in the second chamber observed by them, as the gases are *cooled* near the end walls of the chambers and in the connecting-pipe to the extent of 20° or 30°. In fact, a chamber exposed on the north side to the free air, and on the south side to the radiation from a second chamber, made at the north wall $2\frac{1}{2}$ times more acid 3° Tw. stronger than at the south wall.

There must be a close connection between the temperature at the chamber-wall, the nitrous acid tension, the intensity of the reactions at any given point, and the outside temperature. For every description of chambers, every special place in them, and every rate of manufacture, a certain temperature must be the most favourable—that which causes neither too much nor too little vapour-tension under the given circumstances. More nitre is used when the temperature is too high or too low than under normal conditions [the damage done by too low a temperature is doubtful]. In the case of the "intensive" style of working where the temperature is higher to begin with, any rise of the outside temperature makes less difference. Many manufacturers have adopted this high-pressure style (brought about by a very large supply of nitre, and by ample Gay-Lussac

and Glover space, *cf.* p. 45 *et seq.*), where the draught is better and the cost of plant less; but this can only be done with medium-sized chambers, as otherwise the temperature rises too much at the commencement.

It is obvious how important, in Sorel's view, is the part played by the division of the total chamber-space into several chambers. The cooling-action of the chamber-walls and ends and of the connecting-pipes is also very important. But Sorel does *not* explain why, according to his own showing, the chamber temperature sinks very little in the second half, and very little acid is made there, although the surface of lead on this part of the two long sides and the roof is very much larger than on the two ends and the connecting-pipes taken together.

This seems to prove that the cooling is not the *all*-important factor assumed by Sorel, and that the more intimate mixture of gaseous and liquid particles in the connecting-pipes and the shock against the solid surfaces which brings about a condensation of the particles of mist to larger drops, where the *liquid* substances meet and react upon each other, must be equally acknowledged as potent factors for explaining the anomaly exhibited in the curves, Figs. 338 and 339, p. 964, Lunge's fourth edition. In Lunge's proposals for modifying the chamber-system, as explained on p. 67 *et seq.*, all the influences for reviving the chamber-process are brought into action,—that of an intimate mixture, of the shock against solid surfaces, and of the dilution of the acid by water, which at the same time serves as a cooling agent; and many years' practice has now proved the efficiency of those proposals.

Ostwald[1] has pointed out that the nitrous vapours in the lead-chamber process act merely as catalysing agents, by greatly increasing the speed of the otherwise very slow and incomplete reaction: $SO_2 + O + H_2O = H_2SO_4$. Of course, no objection can be made against extending the class of "catalytic processes," with which it is necessary to deal when speaking of the manufacture of sulphur trioxide (*cf.* volume on *Sulphuric Acid by Contact Processes*, by F. D. Miles), so as to embrace the vitriol-

[1] At the Congress of Electrochemists in 1895 and the German Naturforscher-Versammlung in 1901; *Grundriss der allgemeinen Chemie*, 3rd ed., p. 516.

chamber process as well. As Lunge has shown in *Z. angew. Chem.*, 1902, p. 148 *et seq.*, however, it would be a grave error to imagine that this (or any other) process is explained by calling it "catalytic," or that by giving it that name it is possible to ignore the minute investigation of the *intermediary reactions.* On the contrary, only the latter can lead up to a real "explanation" of the process. In the present case Ostwald's enunciation has caused some little mischief, as others (including Th. Meyer), on the alleged authority of that eminent theoretical chemist, believed they might neglect as unessential the intermediate reactions between the nitrogen oxides and the other substances present. Ostwald himself did *not* go so far; he simply said that the assumption of intermediate products is not suitable for all cases, and that proof should be given that intermediate reactions in fact proceed more quickly than the direct reaction. *In the present case this proof is abundantly afforded by the experience of many generations, and is constantly repeated by every teacher of chemistry.* While the formation of sulphuric acid by the direct action of SO_2 on air and water is notoriously an extremely slow and incomplete process (p. 307), every lecturer on chemistry shows the *instantaneous* formation of chamber-crystals when the above reagents meet with nitrous vapours, and the equally *instantaneous* decomposition of these crystals when meeting an excess of water. A more complete fulfilment of the condition demanded by Ostwald cannot be conceived, or a more utter *reductio ad absurdum* of those who would henceforth consider the reactions of the nitrous vapours in the lead-chambers as unimportant "by-reactions," the study of which is not essential for arriving at a theory of the chamber-process.

Several subsequent papers on the theory of the vitriol-chamber process are given in Lunge's fourth edition, p. 1009 *et seq.*

Brode[1] considered how he could apply the known results of chemical dynamics to the lead-chamber process, but later agreed with Lunge that where hydrated sulphuric acid is *practically completely* formed at a maximum temperature of 90°, the laws of chemical equilibrium cannot be applied. The laws of the velocity of reactions only can be applied. Elsewhere an

[1] *Z. angew. Chem.*, 1902, p. 1081.

increase of velocity is always noticed with increasing temperature; how, then, can a complete reaction have an *optimum* of temperature? The explanation is that the pseudo-catalytical action of the nitrogen oxides in the chamber is founded on two intermediate reactions of different velocity. In such cases, the time required by the entire reaction always depends upon the slower of the intermediate reactions. Since in the lead-chamber water is always present in the form of mist, the process goes on in two phases, the liquid and the gaseous. With an increase of temperature more and more aqueous mist is changed into steam. But nitrososulphuric acid requires *liquid* water for its decomposition, so that with the decreasing amount of the latter, the velocity of one of the intermediate reactions must also decrease. Moreover, this reaction is incomplete with low concentrations of water. This is, therefore, an interesting case of pseudo-catalysis. The direct reaction is practically not reversible, nor is the first of the intermediate reactions,[1] but the second of these (the decomposition of nitrososulphuric acid by water) is reversible. Consequently, after some time nothing remains of the original SO_2, but part of the SO_5NH will remain undecomposed, since for practical reasons, sufficiently elucidated in the text of this chapter, it is not feasible to employ in the last chamber a sufficient excess of water to completely decompose the nitrososulphuric acid. Thus a considerable quantity of the latter must remain up to the last, and it would be removed with the inert nitrogen and oxygen if it were not retained by the Gay-Lussac tower. This theory has explained the reason of the fact, known to practical acid-makers for more than half a century, that there must be a large excess of nitrogen oxides in the last chamber if the conversion of SO_2 into H_2SO_4 is to be practically complete.

Since in the lead-chamber, as in every heterogeneous process, the velocities of condensation and absorption also essentially influence the total velocity, the reactions in the chamber are very complicated and are not yet accessible to mathematical treatment; hence a dynamical theory of the formation of sulphuric acid in the lead-chamber cannot yet be established.

[1] *Cf.* (p. 262 of Vol. I) Lunge's observations as to the great stability of nitrososulphuric acid in the absence of water.

A very important paper on the physical chemistry of the lead-chamber process is that published by Trautz.[1] He declares the mode of action of the nitrogen oxides in the chamber to be still unexplained from the physico-chemical standpoint; he has made experiments for filling up the gaps, and gives a critical review both of his own results and of former attempts in that direction.

Divers[2] tries to reconcile the views of Lunge and Raschig, by making them parts of a more comprehensive theory, according to which, the production of sulphuric acid in the lead-chamber is due to action going on between the liquid and the gaseous parts of the mist, brought about by the momentary intervention of the two catalysts, nitrososulphonic acid and nitrososulphuric acid, $ON.SO_3H$ and $ON.O.SO_3H$. The liquid particles of the mist, consisting of strong sulphuric acid holding nitrososulphuric acid in solution, continuously absorb SO_2 and oxygen, which by the catalytic action of the nitrososulphuric acid are converted into sulphuric acid as fast as they are absorbed. In the normal working of the process, water is taken up in sufficient quantity to effect incipient hydrolysis of the nitrososulphuric acid into its constituent acids. Two molecules of SO_2 and one molecule of O_2 are absorbed simultaneously, for the reason that they find between themselves the radical of the catalyser, nitrosyl, one moment as nitrososulphuric acid, and the next moment as nitrososulphonic acid. Or, leaving out all mention of the radical, nitrosyl, but remembering that the substance of the same formula, nitric oxide, NO, plays no part, the catalyser is nitrososulphonic acid and nitrososulphuric acid alternately.

Raschig, in his first paper of 1904, principally defends his formerly published views against the objections made against them by Divers. He gives reasons for assuming that free sulphurous and nitrous acid combine almost exclusively in molecular proportions to form dihydroxylaminesulphonic acid, $(HO)_2NSO_3H$ or nitrososulphonic acid, $ONSO_3H$, which comes to the same thing. Only a very great excess of SO_2 leads to the formation of the second stage, $HON(SO_3H)_2$, or the third

[1] *Z. physik. Chem.*, 47, 513-610, abstracted in *Chem. Centr.*, 1904, 1, 1301.

[2] *J. Soc. Chem. Ind.*, 1904, p. 1178 *et seq.*

stage, $N(SO_3H)_3$. The process may be represented by the following equations :—

1. $ON.OH + SO_2 = ON.SO_2.OH$,
2. $ON.SO_2.OH + ON.OH = 2NO + HO.SO_2.OH$,
3. $2NO + O + H_2O = 2HO.NO$.

Lunge [1] objects to Raschig's theory, since Raschig discourses on his assumed nitrososulphonic acid and many other compounds never met with in a lead-chamber, and entirely omits to mention two compounds, found in large quantities in the chambers, viz., nitrogen peroxide, NO_2, and nitrososulphuric acid, $ONO.SO_2.OH$, which, if Raschig's theory were right, would do great damage by locking up nitrogen in a useless form. Raschig's principal error is, that he neglects the very first postulate of the law of mass action, viz., the effect which the presence of an enormous amount of free oxygen must have in the action of SO_2 on nitrous acid. This excess of oxygen prevents even the temporary formation of nitrososulphonic acid, instead of which nitrososulphuric acid is formed; Raschig's third equation, $2NO + O + H_2O = 2HO.NO$, is wrong, for NO with oxygen in excess and water is quantitatively transformed into HNO_3. It is only in the presence of, and in direct contact with, sufficient concentrated sulphuric acid that the oxidation of NO does not proceed beyond the nitrous state. Nitrososulphuric acid is always formed quantitatively, but no free nitrous acid is produced.

The next paper is again by Raschig.[2] He does not believe that nitrososulphuric acid occurs in large quantities in the lead-chambers, or that it is at all necessary as an intermediate product for the formation of sulphuric acid. The occurrence of NH_3 in the chambers he takes to be exclusively explicable by his own theory of the formation of nitrososulphonic acid, which he holds to be certain, although that acid has not yet been obtained in the free state.

Lunge, in his reply,[3] refers to the valuable paper of Trautz,[4] in which nitrososulphuric acid plays a principal part, the entirely hypothetical nitrososulphonic acid being set aside. The reduction of nitrites by sulphites to NH_3 is an old-

[1] *Z. angew. Chem.*, 1904, p. 1659 *et seq.*
[2] *Ibid.*, 1904, p. 1777.
[3] *Ibid.*, 1905, p. 60 *et seq.*
[4] *Cf. supra*, p. 328.

established reaction in the manufacture of caustic soda, and therefore the occasional occurrence of traces of NH_3 in a lead-chamber cannot have the importance attributed to it by Raschig, for if that chemist's theory were true, NH_3 must be found in large quantities in the chambers, as the final product of his chain of reactions.

The next paper of Raschig's[1] is summed up by himself as follows. (1) Nitric oxide, when it meets oxygen, is quickly converted into nitrogen trioxide, N_2O_3, and this is slowly further oxidised into nitrogen dioxide, NO_2 or N_2O_4. The times occupied by these two reactions are in the proportion of 1 : 100. [Raschig admits that this contention involves the validity of Avogadro's law, and he is bold enough to say that that law must be considered as being annihilated by his investigations.] (2) In the atmosphere of the lead-chambers it takes three seconds to oxidise NO to N_2O_3, and four minutes to carry on the oxidation as far as NO_2. Since it is unlikely that in the lead-chambers molecules of N_2O_3 and SO_2 meet so rarely that the former have time to oxidise into NO_2, it is necessary to assume that N_2O_3 is that oxide of nitrogen which reacts with SO_2 in the lead-chamber. (3) The same conclusion is reached when observing the behaviour of N_2O_4 and N_2O_3 to SO_2 in the presence of water. N_2O_4 does not act at all on SO_2, but is dissolved as a mixture of HNO_3 and HNO_2, of which only the latter reacts with SO_2. N_2O_3, however, combines directly with SO_2. Hence 1 mol. N_2O_3 converts more SO_2 into H_2SO_4 than 1 mol. N_2O_4. (4) N_2O_3 and nitrous gases of similar composition are quickly, and without causing errors, dissolved by strong sulphuric acid, the analysis of the solution showing the composition of the gases. (5) The compound formed on dissolving N_2O_3 in sulphuric acid, known of old as "chamber-crystals," has not the constitution of nitrososulphuric acid, $O=N-O-SO_2-OH$, but it is nitro-sulphonic acid,

$$\begin{matrix} O \\ \diagdown\!\!\diagdown \\ \quad N-SO_2-OH, \\ \diagup\!\!\diagup \\ O \end{matrix}$$

in which the sulphur is attached to nitrogen. (6) In the action

[1] *Z. angew. Chem.*, 1905, p. 1281 *et seq.*

of reducing agents on nitrosulphonic acid an atom of hydrogen is taken up, and it is converted into nitrosisulphonic acid,

$$O=N\begin{matrix}-OH\\-SO_2-OH.\end{matrix}$$

This acid is soluble in concentrated sulphuric acid with a fine blue colour; in weaker sulphuric acids it produces only a slight red colour which, on addition of a few drops of cupric sulphate solutions, changes into vivid purple. Nitrosisulphonic acid is very easily split up into NO and H_2SO_4. The estimation of nitrogen in Lunge's nitrometer is based on the formation and decomposition of this compound. In his fourth edition (p. 1022), Lunge points out that the formula given for this "nitrosisulphonic acid" involves the assumption of quadrivalent nitrogen. (7) Nitrosisulphonic acid is also formed when SO_2 meets with nitrosulphonic acid, but only when this has been previously split up into nitrous acid and sulphuric acid. It is therefore not formed by a reduction of nitrosulphonic acid, but by the fact that the nitroso-sulphonic acid, $ONSO_3H$, previously formed from a molecule of nitrous acid and a molecule of sulphurous acid, is immediately transformed with a second molecule of sulphuric acid into nitric oxide and nitrosi-sulphonic acid. (8) Exactly in the same way nitrosulphonic acid in the Glover tower yields first nitrous acid, then nitroso- and nitrosi-sulphonic acid, and ultimately nitric oxide and sulphuric acid. The nitric oxide is again oxidised into nitrous acid, which again combines with sulphurous acid, and again yields nitric oxide and sulphuric acid as final products. (9) The same cycle of reactions is continued in the lead-chambers. Both the chamber-process and the formation of sulphuric acid in the Glover tower are expressed by the equations:—

1. $ON.OH + SO_2 = ON.SO_2.OH.$
2. $ON.SO_2.OH + ON.OH = NO + ON\begin{matrix}-OH\\-SO_2.OH.\end{matrix}$
3. $ON\begin{matrix}-OH\\-SO_2.OH = NO + H_2SO_4.\end{matrix}$
4. $2NO + O + H_2O = 2ON - OH.$

The first of these reactions is reversible. If it has taken place, the second follows immediately. The third goes on all the

more quickly, the higher the temperature ; it may entirely cease during disturbances in the chamber-process, especially when the reactions 1 and 2 are continued up to the cool Gay-Lussac tower ; in that case the acid flowing from that tower shows a pink colour. The fourth reaction, at ordinary temperatures, requires three seconds for its completion ; at the higher temperature of the chambers probably even less. (10) This whole theory, Raschig claims to be essentially the same as that which he propounded in 1887 and again affirmed in 1904. Only his former second equation, which he himself in 1904 admitted to be somewhat uncertain, is now separated into two equations, Nos. 2 and 3, each of which he claims to have proved as correct.

In the *42nd Report on Alkali Works*, for 1905, p. 19, where Raschig's paper is mentioned, it is stated that, in Great Britain, experience has abundantly proved that it is practically impossible to avoid disorganisation of the chamber-process when working with a notable excess of SO_2 in the last chamber ; it is most difficult to control the amount of such excess within the limits desired, and escapes from the exit of the process beyond those prescribed by the statute are then most liable to occur. The aim of most acid-makers of experience has been to reduce such excess of SO_2 to a minimum consistently with preserving the lead work of the back chambers from attack by nitric acid, which is a reaction product under conditions of absence of SO_2.

The preceding publication of Raschig's caused Lunge, this time in conjunction with Berl, to take up that subject again. The results of their work in that field are contained in the *Z. angew. Chem.*, 1906, pp. 807 - 819, 857 - 869, and 881 - 894. They proceed to discuss the formation of nitrogen trioxide, N_2O_3, and its existence in the gaseous state. They point out how monstrous is Raschig's attempt at brushing away the physical proofs for the splitting up of N_2O_3 into NO and NO_2 on vaporisation, and his maintaining the formation of N_2O_3 from NO and O by the bold words : "Avogadro's hypothesis is, therefore, false." That means denying one of the fundamental laws of physics and chemistry, which involves also a denial of the kinetic theory of gases and of the modern theories on dissociation, and is absolutely irreconcilable with the work

of so many investigators in that field. The reader is referred for details to the original paper.

In previous editions, full details will be found of the long controversy as to whether or not nitric oxide could be oxidised direct to nitrogen peroxide. The work of Bodenstein [1] proves conclusively that nitric oxide does oxidise directly to nitrogen peroxide. This is confirmed by E. Briner and Fridöri.[2]

The physico-chemical study of the chamber-process is dealt with by M. Forrer,[3] who states that in order to investigate the reactions which take place in the chamber-process, and to determine the temperature coefficient, the apparatus used was such that the five chief gases present during the course of the reaction (sulphur dioxide, nitrogen peroxide, water vapour, oxygen and nitrogen) were used in mixtures of known composition, which could be varied at will. These mixtures were passed at a known rate into a chamber of known dimensions at a definite temperature, each of these factors being susceptible of variation.

Numerous experiments were carried out, and in each case the quantity of acid produced was measured and the acid itself analysed. The author shows that formation of acid only takes place in presence of a liquid phase, so that the time of formation is decreased and the yield increased by the preliminary addition of a small quantity of liquid, in order to start with a heterogeneous system. This liquid should be sulphuric acid itself, as water evaporates and the presence of water vapour is not sufficient to bring about the formation of acid. Under certain conditions the acid itself disappears, this being due to reversal of the reaction; these conditions, however, are different from those obtained in industry. For low concentrations of gas there exists an optimum rate of intake for water; this gives the highest yield and, at the same time, the most concentrated acid. As the gas concentration increases this optimum rate shifts in the direction of diminution of water supply. When the concentration of the liquid phase is constant, the relation between the velocity of the reaction

[1] *Bull. Soc. Chim. Belg.*, 1922, 31, 254-293; *Soc. Chem. Ind.*, 1922, p. 809A.

[2] *Zeit. f. Elektrochem.*, 1918, 24, 183.

[3] *Helvetica Chim. Acta*, 1918, 1, 181.

and the concentration of the gaseous phase is much less complex than in the case when the liquid phase is of varying concentration. The rate of supply of sulphur dioxide does not appear to influence the reaction velocity; on the other hand, nitrogen peroxide and water both exert considerable influence.

The results point to the formation of an intermediate substance, of which water is a constituent, but which is decomposed by an excess of water. Under industrial conditions, *i.e.* in the production of chamber-acid, the rate of intake of water is exactly that which corresponds to the optimum reaction velocity.

Investigations of the formation of sulphuric acid by the chamber-process, by E. Briner and M. Rossignol, are given in *Helv. Chim. Acta*, July 1923, pp. 594-597.

CHAPTER IV

THE PURIFICATION OF SULPHURIC ACID

COMMERCIAL sulphuric acid, as it is produced in the chambers, always contains a number of impurities, derived partly from the raw material, especially the pyrites, partly from the nitre, the water, the lead of the chambers, etc. If the acid is to be purified, this is usually done at the stage now reached, viz., either as Glover or as chamber-acid, and this subject will now be dealt with. In the great majority of works, however, the acid is never purified, nor is there any occasion for it. For the sake of completeness, the manufacture of pure distilled oil of vitriol will be described here also, although this already presupposes the concentration of acid on a large scale.

The impurities of chamber-acid may consist of:—arsenic acid, arsenious acid, antimonic oxide, selenium, thallium, lead, zinc, iron, copper, mercury, calcium, aluminium, alkalies; also hydrochloric acid, sulphurous acid, nitric acid, nitrous acid, nitric oxide (in the presence of ferrous sulphate), fluorine, organic substances.

Most of these substances occur in the acid in too small a quantity to be injurious, and they are also without any influence for most uses of sulphuric acid. The lead is almost entirely precipitated on diluting the acid, and the iron during its concentration, in the form of pink crystals of anhydrous ferric sulphate. But there are cases where these impurities may cause trouble. Thus, according to Deutecom,[1] a minute quantity of *mercury* makes sulphuric acid less suitable for pickling brass objects. *Nitric acid* causes wool to be stained yellow in the "carbonising" process. *Arsenic* and *chlorides*

[1] *Chem. Zeit.*, 1892, p. 574.

render the acid unsuitable for electrical storage-batteries. *Iron* sometimes causes a pink colour, which is removed by a little nitric acid, sometimes even by the action of atmospheric air. [This looks as if the pink colour in such cases was not caused by iron, but by *selenium*.] F. Schultz[1] found that refined white petroleum, when agitated with concentrated sulphuric acid containing SeO_2, turns yellow, all the more so the more acid is employed. In this way, as little as 0·005 per cent. SeO_2 can be detected in sulphuric acid, by shaking it up with petroleum, which thereby turns black, but nitric or nitrous acid causes this reaction even more intensely. Benzol or benzin (0·730 sp. gr.) do not show it; in the case of petroleum probably an oxidising action takes place.

The only two impurities which cause much trouble for many applications of sulphuric acid are *arsenic* and *nitrogen acids*, and most methods of purification therefore aim at the removal of these substances.

Apart from the cases where impurities are at least partially removed from sulphuric acid in the manufacturing process itself, *e.g.* the constituents of flue-dust by the Glover tower, the iron, the crusts forming in the concentrating apparatus, etc., special purifying processes are sometimes employed either because some impurity (*e.g.* arsenic) occurs in an unusually large quantity, or else because very pure acid is required for special purposes. Different methods must be employed for different cases, but the most important of these refer to the removal of arsenic and of the nitrogen compounds. If acid is treated for the removal of arsenic by H_2S, nearly all the other impurities are removed at the same time.

Frequently sulphuric acid is *muddy*. A very slight quantity of lead sulphate and especially of selenium may cause this, nor is the muddiness always prevented by dust-chambers. The removal of the mud is easily effected, down to a residue of about three milligrams per litre, by making the acid slowly traverse several chambers, if possible in a zigzag course. Coarser solid matters may be removed by sand-filters, but these frequently do not effect a clarification of sulphuric acid from selenium or other very finely divided substances. This is such a frequent case that many buyers do not object to the

[1] *Chem. Zeit.*, 1911, p. 1109.

turbid appearance of the acid, which in reality does not interfere with its use in the great majority of cases. Good filters for turbid sulphuric acid, capable of thoroughly clarifying it, are rarely met with.

Arsenic is rarely found, and never in more than insignificant traces, in acid which has been made from brimstone : most of the latter material, indeed, is used where acid free from arsenic is wanted. Spent oxide gives an acid containing 40 to 50 parts of As per million. Blende also contains very little arsenic (*cf.* p. 126 of Vol. I). On the other hand, most descriptions of pyrites contain arsenic, as appears from the analyses quoted in Chapter II, Vol. I, and the acid obtained from pyrites is therefore arsenical, but in very different degrees, according to the percentage of arsenic in the pyrites and to the mode of manufacture.

The percentage of arsenic in pyrites varies greatly. Most analyses of the ordinary ores only show "traces," but up to 1 per cent. and over may occur.

P. Parrish [1] states that from his investigations and experience it would appear that 30 per cent. of the arsenic in an ore is found in the chamber-acid, 20 per cent. in the cinders remaining unvolatilised, and about 50 per cent. in the Glover-tower acid. Of course, the Gay-Lussac acid contains about the same percentage as the Glover acid as the result of constant circulation, and its origin is directly attributable to the Glover acid. Several analyses of the mixed chamber-acids showed a content of 0·17 per cent. of As_2O_3 and ·029 per cent. of As_2O_5, Seville ore being the source of sulphur.

Stahl,[2] in working Spanish pyrites, found in the acid of the first chamber 0·16 per cent. As_2O_3, in the second 0·01 per cent., in the third 0·007 per cent., and in the last chamber only a trace. When working purer pyrites from Virginia or New England, the acid of the first chamber contained 0·005 per cent. As_2O_3, the second nothing, the average 0·002 per cent., all calculated on acid of 66° Bé.

Of course, even with the same raw material, the arsenic in the sulphuric acid will vary, according to whether the gas-pipe leading from the burners to the chambers offers more or less

[1] *J. of Gas Lighting*, 1916, p. 535 *et seq.*
[2] *Z. angew. Chem.*, 1893, p. 54.

opportunity for depositing arsenical flue-dust. In presence of a Glover tower, the chamber-acid contains rather less arsenic, because a large portion of it is deposited at the bottom of the tower in the form of mud, but the acid from the tower itself may occasionally contain all the more arsenic.

At the Freiberg smelting-works, where mixed ores containing from 2 to 2·5 per cent. of As are employed, about 97 per cent. of the arsenic is condensed in the large and well-cooled dust-chambers, described (*cf.* Vol. I, p. 44 *et seq.*), so that the acid contains mostly only 0·02 per cent. of As, only exceptionally up to 0·14 per cent., whilst formerly it amounted to 0·25 or even 0·5 per cent.

The acid made from the very pure pyrites found in some localities in the United States (*cf.* Vol. I, p. 95 *et seq.*) is, of course, free from arsenic.

In order to remove the bulk of the arsenic from raw ores before burning, A. Wyporek, and Rheinisch-Nassauische Bergwerk- und Hutten-A.-G. (Ger. P. No. 331068 of 1919) heat them to a high temperature whereby the arsenic is volatilised with very little loss of sulphur.

O. Nydegger[1] states that the separation of arsenious oxide from the gases from pyrites burners is only possible at temperatures not exceeding 100°, as above this temperature the oxide exerts an appreciable vapour pressure. If the dust-free gases are absorbed in sulphuric acid, the vapour pressure of the arsenious oxide in solution is less, and separation may be effected by this means up to a temperature of 200°.

The author considers that it would be possible to base on the sulphuric acid method, a technical process for the extraction of arsenious oxide from the hot gases before they traverse the Glover tower.

On the *detection* and *estimation* of arsenic in sulphuric acid, *cf.* Vol. I, p. 280 *et seq.*

Injurious Action of the Arsenic contained in Sulphuric Acid.—In most cases where sulphuric acid is employed, a small percentage of arsenic is of no consequence—for instance, in superphosphate, or in sulphate of soda to be used for alkali- or glass-making. Probably sulphuric acid, when employed for

[1] *Bull. Féd. Ind. Chim. Belg.*, 1922, 2, 12-15; *J. Soc. Chem. Ind.*, 1923, p. 11A.

these operations, is never subjected to a purifying process. In alkali manufacture most of the arsenic passes over into the hydrochloric acid and can be traced there. When the hydrochloric acid is used for generating chlorine, the arsenic does no harm; for although it probably passes over, at any rate partly, into the chloride of lime, it will only occur in this as the insoluble and innocuous calcium arsenate. Much more harm is caused by arsenic in the sulphuric or hydrochloric acid which is employed in the food-industries, for instance in the manufacture of sugar-starch, of tartaric acid, in the fermentation of molasses, for pressed yeast, for washing the regenerated char of sugar-work, etc. A. W. Hofmann has reported a poisoning case in which bread was contaminated with arsenic by the use of soda and arsenical hydrochloric acid to make the dough rise.

For some purely technical uses also, arsenic in sulphuric (or hydrochloric) acid is not allowable; for example, for the preparation of certain colours, for tinning iron (sheet-iron cleaned with arsenical sulphuric acid is here and there covered with spots of reduced arsenic, which will not take the tin coating —see Gossage in *Hofmann's Report by the Juries*, 1862, p. 12). According to Falding[1] about 150,000 tons of acid 60° Bé. are used in the United States for the pickling of iron previous to galvanising or tinning, and this acid must contain less than 0·002 per cent. of arsenic. Neither is arsenic allowable in acid used for the manufacture of preparations which serve for food or medicine, and into which a portion of the arsenic might pass. To these belong tartaric, citric, phosphoric acids, glucose,[2] milk of sulphur, sulphide of antimony, etc. It has also been observed that ammonium sulphate made from ammoniacal gas-liquor by means of strongly arsenical sulphuric acid turns yellow, no doubt in consequence of the formation of sulphide of arsenic. Parrish[3] mentions three methods for overcoming this difficulty: (1) Working with a film of oil or of anthracene on the

[1] *J. Soc. Chem. Ind.*, 1906, p. 403.

[2] It is only necessary to point to the "beer-scare" of 1900, consequent upon the mischief done by drinking beer brewed with addition of glucose which had been prepared by means of sulphuric acid with an extraordinarily high percentage of arsenic, some of which remained in the glucose.

[3] *J. Gas Lighting*, 1916, p. 134; abstr. *J. Soc. Chem. Ind.*, 1916, p. 535.

surface of the acid in the saturator, which film retains both tarry substances and sulphide of arsenic. This method is used by shale distillers in Scotland. (2) Using a closed saturator with an automatic scumming device; the arsenic sulphide is discharged continuously with the tarry matter, without the use of an oil film. (3) Precipitating the arsenic from the acid by means of the waste gases from the saturator, containing H_2S. An apparatus for doing this in a continuous way is described in the original.

Removal of Arsenic from the Acid.

In some cases, therefore, it is of importance for the producers of strongly arsenical acid to make it more saleable, and a number of methods of purification have been proposed with this object. None of them seems to produce an acid absolutely free from arsenic, but they are sufficient for all practical purposes. Bloxam,[1] by employing his electrolytic method for the detection of arsenic, found that all samples sold as "chemically pure" contained traces of it, and that acid absolutely free from arsenic cannot be obtained in any other way than from pure sulphur dioxide and nitric oxide in glass apparatus at a low temperature, avoiding all cork or india-rubber; the gases themselves must be evolved cold or at a very moderate temperature.

Sulphuric acid dissolves arsenic even out of the glass bottles in which it is stored.

(1) By *Partial Deposition in the Manufacturing process itself.*—Hardwick[2] reports a very curious case of the injury caused by burning pyrites with an unusually high percentage of arsenic (1·7 per cent.). Every part of the plant showed the presence of arsenious oxide or acid. The acid from the Glover tower deposited large quantities of As_2O_3 in the shoots, connecting-pipes, acid-eggs, cisterns, and, worst of all, in the Gay-Lussac tower, where the coke was ultimately so choked up with it that the works had to be stopped. After many fruitless attempts to remedy this nuisance, the most effectual method for loosening the deposits of arsenious oxide was found to be the application of steam. To prevent the renewed

[1] *Pharm. J.*, [2], 3, 606. [2] *J. Soc. Chem. Ind.*, 1904, p. 218.

formation of these deposits, it is not sufficient to allow the Glover tower acid to cool and clarify by settling out the mud. Better results were obtained by heating the acid with strong nitric acid which oxidises the As_2O_3 to As_2O_5, the latter being soluble in strong sulphuric acid. This treatment was carried out in special tanks, provided with a steam-coil for heating and a water-coil for cooling, where the Glover tower acid, after previous settling out of all the mud removable, was heated up to 82°; the theoretically necessary quantity of nitric acid for oxidising the As_2O_3 to As_2O_5 (as shown by an estimation of the As_2O_3 by means of iodine solution) was added, with good agitation, and the liquor cooled down with occasional agitation. In that way, it became possible to work highly arsenical ore without any stoppages of the plant, at a slight cost.

The Gräflich von Landsberg Chemische Fabrik, etc. (Fr. P. 432874), oxidises the As_2O_3 in the gases to the non-volatile As_2O_5, which is removed by washing the gases with acid before they enter the chambers. First the dust is removed by filtration through vertical chambers with sloping bottoms, filled with granular material which can be withdrawn below and replenished from above. The gases then pass through one or more Glover towers and then through washing-towers to the chambers, the acid running from the washing-towers being sent finally to the first Glover tower (see p. 454 of Vol. I).

The following methods have been employed for the separation of arsenic from sulphuric acid :—

(2) *Distillation* of the sulphuric acid[1] is said to effect this purpose even more completely than precipitation by sulphuretted hydrogen, provided that the arsenic is all present as *arsenic acid*, which remains behind in the residue ; if, however, arsenious acid be present, it is carried over with the sulphuric acid. Since the sulphuric acid of commerce mostly contains arsenious acid, it should be treated with nitric acid in order to convert all the arsenic into arsenic acid. Then the acid must be mixed with a little ammonium sulphate (in order to destroy the nitrous acid) and distilled. In this case, it is asserted that the arsenic is removed more completely than by sulphuretted hydrogen or barium sulphide. At the same time the dilution of the acid, necessary in the latter case, is avoided. But the

[1] Bussy and Buignet, *Dingl. polyt. J.*, 162, 454.

distillation of sulphuric acid is an operation somewhat difficult on the large scale, and is not applicable for the purification of chamber-acid.

According to Blondlot,[1] the employment of ammonium sulphate is unsuitable, because an excess of it again reduces arsenic acid. He therefore recommends heating the acid with peroxide of manganese or potassium permanganate. Bussy and Buignet deny that an excess of ammonium sulphate reduces arsenic acid.[2] Maxwell Lyte[3] says the statement of Bussy and Buignet, that arsenic does not distil over unless present as arsenious acid, is correct; but in order to obtain a product completely free from nitrogen compounds, he destroys the latter by adding to the sulphuric acid $\frac{1}{4}$ to $\frac{1}{2}$ per cent. of oxalic acid, heating in a porcelain dish to 110° with continuous stirring, cooling down to 100°, and adding potassium bichromate in the state of powder or as a solution in sulphuric acid, till the green colour has been changed to greenish yellow and the presence of free chromic acid is thus indicated. All the arsenic is now converted into arsenic acid, and on distillation a perfectly pure acid is at once obtained. Permanganate of potash acts in the same way but is more expensive.

(3) *Removal by Crystallisation of the Sulphuric Acid.*—Morancé[4] makes use of the fact, established by Lunge, that sulphuric acid of 65°·5 to 65°·8 Bé. crystallises at −20° in a pure state. He concentrates the acid taken from the Glover tower to about 63° Bé., and allows it to stand at a temperature from −8° to +2° for twenty-four hours, when about half of the acid will have crystallised out. The crystals are decanted and centrifuged. The following table shows the decrease of the impurities by this process:—

	Crystals.	Mother Liquor.
Ash	0·281	0·829
Iron and aluminium . .	0·029	0·119
Arsenic	0·033	0·368

This shows, however, that no *complete* removal of arsenic is effected by this process.

[1] *Comptes rend.*, 58, 76. [2] *Ibid.*, 58, 981.
[3] *Chem. News*, 9, 172. [4] *Comptes rend.*, 148, 842.

(4) *Removal as Trichloride.*—Arsenic trichloride boils at 125°; it is therefore completely volatilised on heating, long before the sulphuric acid has begun to boil. This process can be used without diluting the acid (which is in some cases a great advantage compared with the removal of the arsenic as sulphide). With this object Otto and Löwe proposed heating the acid with common salt;[1] Graeger, heating with barium chloride, because the action in this case is not so rapid.[2] Buchner (in 1845) recommended conducting a current of hydrochloric acid gas into boiling sulphuric acid, and expelling the hydrochloric acid by heating in the air. Bussy and Buignet have proved that in this way, acid free from arsenic cannot be obtained. Buchner, however,[3] asserts that this is due to the presence of arsenic acid, and that an acid entirely free from arsenic is obtained by first reducing the arsenic acid contained in the sulphuric acid by heating it with charcoal, when the sulphur dioxide evolved causes the reduction. This reduction can also be carried out during the passage of the current of hydrochloric acid gas. If Buchner's statement is correct, the troublesome operation of distilling the acid is unnecessary. Schwarz[4] heats the acid for some time with 1 per cent. of common salt and ¼ per cent. of charcoal dust under a chimney with a good draught—which comes to the same thing, and appears to be more convenient; but on carrying it out on a large scale great difficulties arise from the fact that the process does not work with dilute acid. According to Tod,[5] if a current of HCl is introduced, heating to 130° to 140° is sufficient, whilst if common salt is employed, the acid must be heated to 180° to 190°, in order to expel the arsenic trichloride.

In 1905 quite a number of patents were taken out by the United Alkali Company, together with several of their chemists, for the removal of arsenic from sulphuric acid as arsenious chloride, and the treatment of the latter substance for commercial use (B. Ps. 2916, 7916, 16929, 16930, 16931, 17787, 17886; U.S. Ps. 846288, 863940). The acid is subjected, in a suitably packed tower, to the action of dry hydrochloric acid gas, at a temperature of about 100°, preferably as it leaves

[1] *Dingl. polyt. J.*, 132, p. 205. [2] *Ibid.*, 155, 236.
[3] *Chem. Centr.*, 1864, p. 600. [4] Wagner's *Jahresber.*, 1865, p. 232.
[5] Liebig's *Jahresber.*, 1865, p. 292.

the Glover tower. Arsenious acid may be obtained from the chloride by alkalies or carbonates of various metals. B. P. 5151 of 1906, of Raschen, Wareing, Shores, and the United Alkali Co., Ltd., describes reducing arsenic compounds to the arsenious state by charcoal. Their B. P. 23130 of 1906 states that this is a slow process, and the reaction soon ceases, owing to selenium deposited on the charcoal. They now overcome this difficulty by subjecting the sulphuric acid to the combined action of HCl, and either sulphur or charcoal at 100° or below. If there is still some deposition of selenium, this may be removed by washing with hydrochloric acid and an oxidising agent, such as a hypochlorite or a chlorate. The use of sulphur in conjunction with HCl is only possible in the absence of selenium; if selenium is present, charcoal + HCl must be used. Their Fr. P. 363947 suggests mixing the arsenious chloride, obtained as described above, with just sufficient water to precipitate the selenium, which is filtered off; a larger quantity of water is then added to precipitate the arsenious oxide.

Raschen, Imison, and the United Alkali Company (B. P. 30196 of 1909) add to the sulphuric acid, hydrochloric acid in sufficient quantity to convert the arsenic into chloride, viz. 3 mols. HCl to each molecule of $AsCl_3$, or 5 mol. HCl to each molecule of $AsCl_5$, plus an excess for working losses, and maintain such conditions that the Cl corresponding to the pentavalent As escapes as gas, whilst the $AsCl_3$ remains in the sulphuric acid and is removed by blowing with air.

Crowther, Leach, and Gidden (B. P. 20509 of 1907) remove arsenic and selenium by mixing cold sulphuric acid of 140° down to 135° Tw. with a little hydrochloric acid (30 to 32 per cent.), and bringing it in contact with finely divided sulphur for about two hours, whereby the $AsCl_5$ is reduced to $AsCl_3$, which is then removed by blowing a current of air through the liquid. The process may be worked continuously by passing the mixture of sulphuric and hydrochloric acid down a tower packed with sulphur, a current of air being blown through, or SO_2 may be employed instead of sulphur, by subjecting the mixture of sulphuric and hydrochloric acid to a stream of air containing a small quantity of SO_2. The air carrying the $AsCl_3$ and HCl, is first passed into strong hydrochloric acid in order to deposit sulphur and selenium and then into water, to

decompose $AsCl_3$ into strong hydrochloric acid and precipitated As_2O_8.

The Verein Chemischer Fabriken, Mannheim (B. P. 16910 of 1906; Ger. P. 179513), takes out the arsenious chloride by means of hydrocarbons, glycerides, etc., in which it is soluble; mineral oils especially are suitable for this, but not easily decomposable aliphatic glycerides.

The Chemische Fabrik Griesheim-Elektron (B. P. 973 and 974 of 1907; Ger. Ps. 194864 and 195578; Austr. Ps. 32449 and 34022; Belg. Ps. 197391 and 198423; Fr. P. 376934; Ital. Ps. 245/84 and 246/85) converts the arsenic in sulphuric acid into chloride or fluoride and removes it by treating with benzol or with derivatives of benzol or of aliphatic hydrocarbons, such as dichlorobenzene, or carbon tetrachloride, or acetylene tetrachloride. From these solvents the arsenic is separated by washing with water. For instance, sulphuric acid of 66° Bé. containing 0·1 per cent. As is mixed with 0·6 per cent. hydrochloric acid of 27° Bé., or a corresponding quantity of hydrofluoric acid; 10 per cent. carbon tetrachloride is added and stirred up with the acid for a few minutes; it is then removed and contains all the arsenic. When saturated with arsenic, the tetrachloride is treated with twice its weight of water, which takes out the arsenic. This treatment is applied at Griesheim to take out the arsenic from Glover tower acid, upon which great claims are made with respect of colour or smell. It is only applicable to acids over 58° Bé. but does not remove the arsenic from chamber acid, etc. This is, however, effected according to their B. P. 3435 of 1907, by adding, in addition to hydrochloric acid, a little iodine or HI, and then treating with SO_2, which converts the I into HI. The latter reduces any As_2O_5 to As_2O_3, and the iodine formed acts as before, so that by means of very little iodine, up to 80 per cent. of the arsenic can be removed from chamber-acid.

(5) *Removal as a Soap.*—For electrical storage-batteries, sulphuric acid should be as free from arsenic as possible. Arsonval endeavours to attain this by pouring 4 or 5 c.c. of colza oil on to a litre of sulphuric acid, which is to form glycerine-sulphuric acid, and to precipitate the arsenic, lead, etc., in the form of soaps [?]. Gothard suggests the same addition; the mixture is to be shaken up, allowed to stand for

twelve hours, poured into water, and, after cooling, the sticky mud must be skimmed off.[1]

(6) *Precipitation as Sulphide.*—This method, formerly the only one carried out on a manufacturing scale, possesses the advantage that, apart from the arsenic, several other impurities are precipitated (such as lead, antimony, selenium), and others are destroyed (such as sulphurous, nitrous, and nitric acids).

When the arsenic is present as arsenic acid, it is much more slowly precipitated than when present as arsenious acid.

The simplest way might be thought to consist in generating the sulphuretted hydrogen within the liquid itself, and the methods and proposals made for this purpose will be considered first.

(*a*) *Precipitation by Barium Sulphide.* — Proposed by Dupasquier in 1845, this process was carried out practically at Chessy,[2] and it appears to have been used at most of the French works where the acid is purified. In this case, barium sulphate and sulphuretted hydrogen are formed, the latter being in the nascent state and therefore acting very energetically. This process has, moreover, the great advantage of leaving nothing soluble behind in the acid. It has been objected that the barium sulphide must be pure and must contain no thiosulphate, since otherwise the well-known decomposition between H_2S and SO_2 with separation of sulphur takes place. This objection, however, is unfounded, because the barium thiosulphate also precipitates the arsenic as sulphide, and only an excess of it (which ought to be avoided in any case) would cause separation of sulphur.

(*b*) *Sulphide of iron* may be employed in cases where the iron does no harm—for instance, for acid required in the tinning and galvanising of iron, etc. Its application, however, is very limited.

(*c*) *Sulphide of Sodium* is capable of much wider application, although it, too, introduces a foreign substance (sodium sulphate) into the acid. This, however, is innocuous for most uses of the acid. The sodium sulphide must be added to the acid to be purified until no further precipitation takes place. The writer finds this reagent very useful in cases of slight

[1] *Chem. Zeit.*, 1892, p. 163.
[2] *Hofmann's Report by the Juries*, 1862, p. 12.

contamination of acid with arsenic, due to irregularities in the working of the ordinary process of de-arsenication by sulphuretted hydrogen. The filtration of the precipitate will be described later on.

(*d*) *Crude calcium sulphide* (alkali-waste) can be used exactly in the same way as sodium sulphide, and with the same drawback of introducing some fixed impurities, since part of the $CaSO_4$ remains in solution.

(*e*) Thomson (Ger. P. 6215 of 1884) employs *ammonium sulphide* for precipitating arsenic and antimony, and at the same time destroying the nitrous compounds in chamber-acid. He then filters over finely divided lead, and concentrates in the usual manner.

(*f*) *Sodium and barium thiosulphates* are very much recommended; the latter is more expensive, but leaves nothing soluble in the acid. The following is the reaction which occurs:—

$$As_2O_3 + 3Na_2S_2O_3 = As_2S_3 + 3Na_2SO_4.$$

According to W. Thorn[1] sodium thiosulphate is actually used in some works. Chamber-acid of 106° Tw. is heated to 70° to 80°, and the necessary quantity of the reagent, either in solution or as powder, is well stirred up with it. The arsenic sulphide separates in flakes, which soon gather into lumps and sink down to the bottom of the tank. The clear acid is drawn off, and fresh quantities are purified in the same tank, until at last there is too much precipitate collected at the bottom, when it is removed and washed. The operation is very simple, and if an excess of the reagent is avoided, very little sulphur dioxide is evolved. In a particular instance, the average percentage of arsenic in chamber-acid of 106 Tw., before purification, amounted to 0·098 per cent., after purification to 0·004 per cent. The purified acid contains from 0·03 to 0.04 per cent. sodium sulphate, which is harmless for most purposes.

In some cases, the presence of sodium sulphate in the acid is objected to, especially when the strongest acid is to be obtained. It is therefore preferable to employ barium thiosulphate, which is easily obtained by mixing moderately concentrated solutions of sodium thiosulphate and barium chloride; most of the barium thiosulphate is precipitated in a crystalline

[1] *Dingl. polyt. J.*, **217**, 495.

form, and is separated from the worthless mother-liquor on a vacuum-filter. The acid to be purified is heated to about 80°, and is well agitated (which can be most readily done by a stream of air), the requisite quantity of barium thiosulphate is thrown in, and the temperature is kept at 80° to 100° till all the arsenic is precipitated. The reaction is :—

$$As_2O_3 + 3BaS_2O_3 = A_2S_3 + 3BaSO_4,$$

so that nothing soluble is left in the liquid. The mixed mud of arsenious sulphide and barium sulphate settles down very rapidly. It is separated from the acid by decantation or filtration, and washed in order to remove most of the acid. Where the barium sulphate is of some value, it is easily recovered by boiling the mud with milk of lime, when the arsenic is dissolved, and can be reprecipitated from the solution for sale as "yellow arsenical glass," whilst the residue of barium sulphate can be submitted to the usual treatment for the manufacture of barium chloride. This process is actually carried out on a considerable scale, but it is not quite so cheap as the treatment with sulphuretted hydrogen, and does not seem adapted to acids containing a large quantity of arsenic.

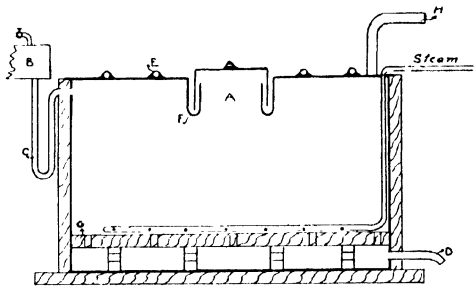

FIG. 158.

(*g*) *By Gaseous Hydrogen Sulphide.*—This process appears first in a patent by W. Hunt (No. 1919 of 1853) and is that which is most usually employed on a large scale.

1. *Generation of the Sulphuretted Hydrogen.* — For this purpose a matte is used, made by smelting together in a reverberatory furnace, smalls (non-cuprous) pyrites, and the requisite amount of scrap-iron (turnings, or the like).

The matte is broken into pieces, roughly about 8 in. or 9 in. diameter, and put into the generator through the manhole A, Fig. 158.

Sulphuric acid, free from arsenic, of about 40° Tw. is

gradually run into the apparatus through the box B and pipe C, so long as the generation of gas is required.

The resultant sulphate of iron is run off at intervals through the outlet-pipe D, into a lower tank provided with a steam-coil, and scrap-iron is used to completely neutralise any free acid contained therein, should the material be required for sale.

The generator is constructed of 3-in. planks securely bolted together, and is lined with 10-lb. lead. The top of the vessel is covered and supported with lead-covered iron cross-bars, E. It is provided with a deep lute, F, in order to avoid escape of the poisonous gas, and to maintain a pressure.

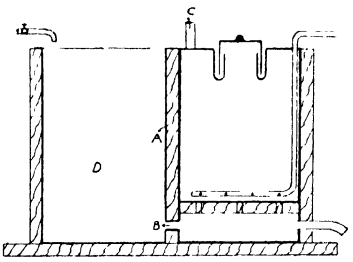

FIG. 159.

The bottom of the tank is preferably arranged with a perforated false tray, G, supported on bricks, and a steam-pipe with ½-in. holes is fitted, in order to prevent crystallisation of the sulphate of iron formed, and to assist decomposition of the FeS. H is the outlet for the gas.

Another type of generator is shown in Fig. 159, and is more suitable for dealing with smaller quantities of gas. The apparatus is divided by the partition A, containing the connection B, for allowing a flow of liquid from one compartment to the other.

When the gas outlet, C, is closed, the acid is forced (by the pressure of the gas) into the compartment D, and the action of the acid upon the FeS thus discontinued.

The generators are preferably built in duplicate, so as to have one apparatus always available, and thus provide a constant supply of gas in case one of the apparatus has to be closed down for cleaning or repairing.

The amount of sulphide of iron used per ton of acid varies according to the arsenic content of same. For acid produced from pyrites containing about 0·5 per cent. of As, the quantity of sulphide used would be about 35 to 45 lb. per ton of acid treated.

Sometimes *explosions* take place during the treatment with hydrogen sulphide. The *41st Report of the Alkali Inspectors*

(p. 19) says that at certain stages an explosive mixture is formed, and several accidents to workmen and to plant have occurred from this cause. This explosive character of the gases is rendered worse by the fact that free hydrogen is given off in the generators from metallic iron contained in the ferrous sulphide employed. Moreover, if either that substance or the sulphuric acid used in the generator contains arsenic, *arseniuretted hydrogen* will be evolved, about the extremely poisonous character of which it is unnecessary to speak.

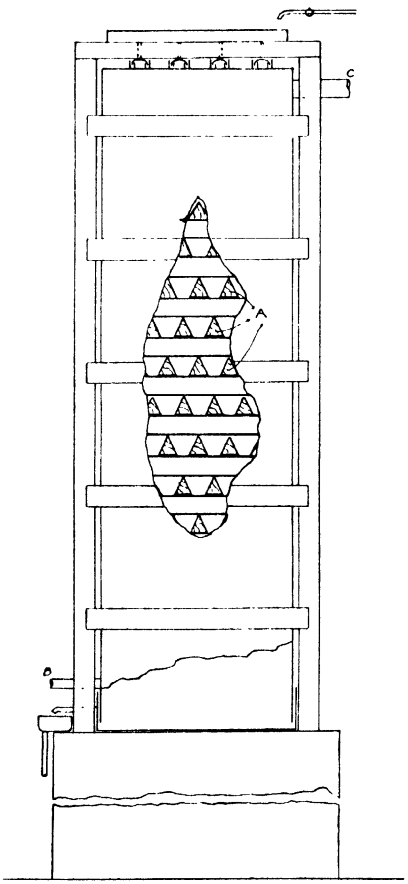

FIG. 160.

2. *Precipitation of the Arsenic in Chamber-Acid.*—The tower used for the above purpose is shown in Fig. 160, and consists of a tower 6 ft. square by 18 ft. high, constructed in the well-known manner of timber-framing, lined with 10-lb. lead. It is filled with tiers of V-shaped inverted lead gutters, 5½ in. high and as wide at the base, made of 10-lb. lead, the lower edge of which may be serrated. Or they may be made from solid triangular lengths of timber, A, covered with 6-lb. lead. The slope of these being greater than the angle of repose for the mud formed in the process, the bulk is carried down to the lower portion of the tower and thence into settling tanks.

A tower of the size mentioned, is capable of dealing with 30 to 40 tons of chamber-acid per twenty-four hours, according to the amount of arsenic present.

The sulphuretted hydrogen enters by the pipe B, and the air and vapour leave at the top, C. These, after passing a wash-bottle, are carried to the steam boiler flue.

The heat generated in the treatment is usually sufficient to increase the temperature of the acid 5° to 10°, thus aiding precipitation.

Of course, constant tests must be made to ensure complete purification in this tower. For ordinary purposes it is sufficient to employ a simplified Marsh test as follows:—Put some of the acid into a 4-oz. bottle, closed with a cork provided with an outlet-pipe drawn out to a point. A few pieces of pure zinc are dropped in, the cork is inserted, the gas issuing is lighted (with the ordinary precautions against an explosion by premature lighting if the gas contains air) and the flame is directed on a slab of porcelain, where no spot of As should be produced. For more accurate observations the methods mentioned (*cf.* Vol. I, p. 280-6) should be employed. If a batch of acid is not found free from arsenic by the above test, it must be pumped up and treated once more, or treated with a solution of sodium sulphide as described above. This test should be repeated by the laboratory chemist before passing a batch as purified, and in cases of any importance, the acid should be tested a third time before being sent out. The above simple Marsh test, or the ordinary Marsh-Berzelius test (heating the gas in a tube, where metallic arsenic is deposited), does not detect the minutest traces of arsenic; but it may be taken that any acid in which these tests do not indicate any arsenic, is "practically" free from arsenic and can be used for all purposes, like acid made from brimstone.[1]

Leroy W. M'Cay[2] proposes facilitating the precipitation of arsenic by H_2S by conducting the operation at 100° under pressure and with agitation. The application of pressure for this purpose is also recommended in *Chem. Trade J.*, 1905, 36, 135.

[1] This is universally done, even for the purpose of manufacturing articles of human consumption, in most countries, where brimstone has not been used in the manufacture of sulphuric acid. No inconvenience seems ever to have been caused by this practice; but since the "beer-scare" of 1900 many people in England demand that no acid should be allowed to be used in the manufacture of articles of food, etc., except that made from brimstone.

[2] *Chem. Ind.*, 1889, p. 371.

Bithell and Beck (B. P. 1500, 1913) run the sulphuric acid through a tower, divided by horizontal diaphragms into several chambers. H_2S is blown into the bottom chamber, and rises upwards from chamber to chamber by serpentine pipes.

G. E. Clark (B. P. 144869 of 1919) describes an apparatus for treating sulphuric acid with sulphuretted hydrogen, which comprises a tower with suitable baffles, through which the acid also flows in a zigzag path. The gas is conveyed under pressure and sprayed by nozzles into a container. After

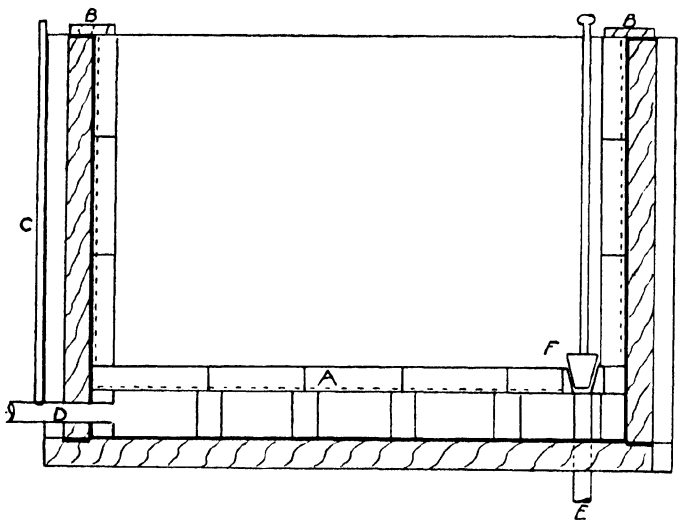

FIG. 161.

passing through the acid in this vessel and effecting its de-arsenication, the gas passes upwards through the tower, and thus brings about a preliminary treatment of a fresh supply of acid.

3. *Filtration.—Filters.* These are made of 3- or 4-in. planks held securely together by strong tie-rods, and are lined with 8-lb. lead. It is very important that these cisterns be strongly built, for any disturbance of the tile-lining may cause faulty filtration. Fig. 161 shows a sectional elevation of a filter.

Several rows of ordinary acid-resisting bricks are placed upon the bottom of the vessel to form draining-space for the filtrate. Upon these, porous tiles (Mackenzie and McLaughlan's), A, are

placed, the joints of which are made of lead-wool well caulked or, by means of silicate of soda and asbestos powder. After the bottom is laid as described, the four sides are built in a similar manner, and, before caulking, a top-rail, B, is firmly attached to prevent movement of the tiles. An air-pipe, C, is provided to allow filtration to proceed, and a discharge-pipe, D, is arranged for running off the clear acid, being provided with a rubber connection and pinch-clamp. Another pipe may be fixed near one side for discharge of the precipitated arsenic, E, with plug F.

From 1 to 3 cwt. of acid of 106° Tw. can usually be filtered per sq. yard per hour with a head of 2 ft. where acid containing an average amount of impurity is being dealt with.

In order to expedite filtration, vacuum may be applied by any well-known means by pipe D. The filters should always be kept supplied with acid in order to prevent cracks forming, for the precipitate acts as a filtering medium for the finely divided sulphur formed from the necessary excess of sulphuretted hydrogen used in the treatment.

The amount of arsenic, varying as it does, has considerable influence upon the rapidity with which filtration takes place.

Taking ordinary chamber-acid produced from the burning of ores containing 0·2 to 0·3 per cent. of As, the yield is about 60 per cent. by volume of clear liquor and 40 per cent. of the precipitate, whilst Glover-tower acid made from the same ore will often yield only 10 per cent. of clear acid. The clear liquor may be decanted or allowed to flow through the porous tiles, and it is then transferred into quartz-filters, and, after filtering again, allowed to run into covered storage-cisterns.

As a precaution, this liquor may be further treated with sulphuretted hydrogen on its way to the stores.

When the filters become half full of sediment, the outlet D is closed, water added, the whole contents well stirred, and the clear liquor decanted or allowed to filter off. When the precipitate is sufficiently washed, it may be removed by flushing it out by the outlet E, and transferred by pressure-vessel to the filter-press, or otherwise dealt with as described below.

4. *Disposal of the Sulphide of Arsenic.*—Instead of washing and filter-pressing the precipitate, the muddy acid can be efficiently dealt with by pouring a little fused paraffin into the

cistern containing it, and stirring up by means of air. With the As_2S_3 the paraffin forms lumps of the consistency of butter, which float on the surface of the acid and are easily ladled off; only an extremely slight trace of paraffin remains behind. The lumps of paraffin + As_2S_3 are treated with a solution of sodium sulphide. The paraffin floats on the top, and can

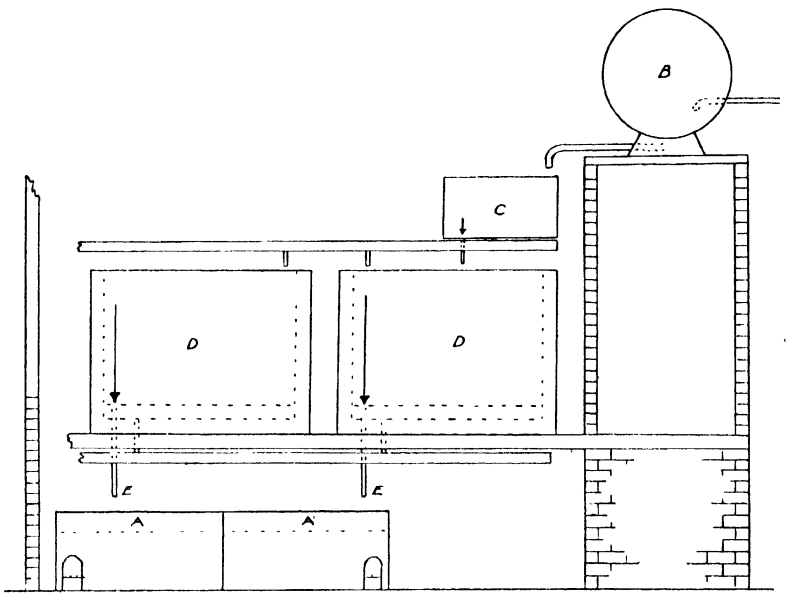

FIG. 162.

always be used over again. The solution of sodium sulpharsenite is decomposed by sulphuric acid, and the As_2S_3 is now easily filtered off. It is washed, dried, and heated to 150°, which causes it to frit together. In this state it goes out for sale.

Another method is to run off the settled mud, without previous washing, into the lead-pans A, Fig. 162, by outlet E, and after heating up for a short time, the sulphide of arsenic separates in hard lumps, almost as hard as a clinker, and only requires draining, when it is ready for disposal. Precautions must be taken, however, to prevent overheating of the pans, the heat being withdrawn the moment the precipitate commences to coagulate.

The following is the analysis of the material produced at the works of which the writer had charge :—

Moisture	10·3 per cent.
Free acid	8·0 ,,
As_2S_3	48·0 to 56·0 ,,
Free sulphur	30·0 to 38·0 ,,
Insoluble	1·5 ,,

G. E. Davis recommends the following process for dealing with the sulphide of arsenic. The mud is warmed up to the melting-point of naphthalene, paraffin, etc., and a little of these substances is added and the mixture well stirred. Afterwards this naphthalene may be distilled off by steam. If paraffin is used, this may be separated by treatment with ammonium sulphide, or in various other ways.

Riley and Barnes (B. P. 25444 of 1901) recover arsenious acid from the arsenious sulphide by heating it to about 160° with nearly its own weight of strong sulphuric acid for some hours. The floating scum of sulphur is removed and washed, and the acid liquor is concentrated to obtain crystallised arsenious acid.

According to the *Chem. Trade J.*, 1906, **38**, 87-88, the sulphide of arsenic, after washing, in a fairly dry state contains :—

	1.	2.
Arsenious sulphide, As_2S_3 . . .	43·02	51·20
Free sulphur	17·03	6·00
Antimonious sulphide . . .	1·11	1·40
Lead sulphide	0·76	0·38
Bismuth sulphide	0·35	0·29
Copper sulphide	0·69	0·22
Ferrous sulphide	1·87	6·02
Calcium sulphide	0·90	0·13
Sulphuric acid	14·20	13·00
Organic substances, insolubles . .	2·01	6·00
Water, etc.	18·06	15·00
	100·00	99·64

It is very poisonous, and should not be put on the waste heap. The small quantity produced at each works sometimes causes considerable difficulty in disposing of it.

According to the same source, p. 90, a sample of ordinary commercial sulphuric acid of 140° Tw. was found to contain :—

	Gram per litre.
Arsenious oxide, As_2O_3 . . .	3·18
Arsenic oxide, As_2O_5 . . .	2·56
Hydrochloric acid, HCl . . .	0·08
Nitrous compounds, N_2O_3 . . .	0·52
Ferrous sulphate	0·56
Aluminium sulphate, $Al_2(SO_4)_3$ . .	0·46
Pb, Zn, Cu, Sb, Bi, Se . . .	traces

De-arsenication of Strong Sulphuric Acid.

T. S. Moore[1] describes some very interesting experiments on the de-arsenication of strong sulphuric acid.

The experiments were carried out at the temperature of the laboratory. Hydrogen sulphide at the rate of one bubble a second was passed through 200 grams of the acid under examination, and the product filtered through asbestos in three separate portions : (1) without any special precaution ; (2) with hydrogen sulphide passing through the liquid while filtering ; and (3) without precaution, after the liquid and precipitated arsenious sulphide had remained together for one or two days.

In de-arsenicating arsenical D.O.V. (95 per cent. H_2SO_4, 0·15 per cent. As_2O_3, 0·11 per cent. As_2O_5) it was found : (1) that the process was slow, taking two and a half hours in laboratory apparatus ; (2) that excessive reduction of sulphuric acid occurred, the strength of the resulting acid being 91·8 per cent. ; (3) that if filtration from the arsenic trisulphide is carried out immediately after the precipitation the arsenic content is 2 to 3 parts As_2O_3 per million, but that the arsenic content is higher the longer the filtration is delayed ; and (4) that if hydrogen sulphide is passed through the liquid during filtration, the arsenic content falls to less than 1 part As_2O_3 per million. Further, under the conditions last mentioned, the acid coming through the filter is perfectly clear, but soon becomes cloudy owing to the precipitation of sulphur, which shows that the rate of oxidation of hydrogen sulphide by strong sulphuric acid is not rapid enough to prevent the accumulation in solution of an appreciable quantity of the gas.

[1] *J. Soc. Chem. Ind.*, 1919, p. 399T.

With arsenical D.O.V. diluted to contain approximately 80 per cent. of sulphuric acid, it was found that: (1) the rate of reduction of the sulphuric acid is quite small. The original acid contained 79·7 per cent. H_2SO_4. After one hour's treatment with hydrogen sulphide, the acid contained 79·4 per cent. H_2SO_4. After two hours' treatment it contained 77·8 per cent. H_2SO_4; (2) acid filtered immediately after one hour's treatment contained 1 part As_2O_3 per million, and the arsenic content was not diminished by passing hydrogen sulphide during filtration; and (3) when filtration was delayed for days the arsenic content had risen only to 1·5 parts As_2O_3 per million. Two days after the acid had been filtered, it still smelt of hydrogen sulphide, which shows that the rate of reaction between hydrogen sulphide and 80 per cent. sulphuric acid is small.

The behaviour of 70 per cent. acid resembles that of 80 per cent., the chief differences being that (1) de-arsenication is slightly more rapid; (2) filtration of the arsenic trisulphide may be delayed several days without any serious increase of the arsenic content; and (3) there is even less reduction of sulphuric acid.

Finally, an experiment with Glover-tower acid of unusually high arsenic content was carried out, in which hydrogen sulphide in fine bubbles was passed through 500 grams of the acid contained in a bottle fixed on a shaking-machine. One hour's treatment with hydrogen sulphide proved insufficient for this acid, and in a second experiment treatment was continued for one and three-quarter hours. Part of the product was filtered immediately and part after two days. The results of analysis were :—

	Before treatment.	After immediate filtration.	After standing two days.
	Per cent.	Per cent.	Per cent.
H_2SO_4 . . .	77·1	77·1	77·1
N_2O_3 . . .	0·18	None.	None.
As_2O_3 . . .	0·29	Between 0·6 and 1 part per million.	2 parts per million.
As_2O_5 . . .	1·58	None.	None.

These figures need some comment, for as they stand they give the impression that there is no loss of sulphuric acid.

The following calculation shows that de-arsenication should actually cause an increase of the sulphuric acid content. The reactions proceeding are :—

$$N_2O_3 + H_2S = H_2O + 2NO + S;$$
$$As_2O_3 + 3H_2S = As_2S_3 + 3H_2O;$$
$$As_2O_5 + 5H_2S = As_2S_3 + 5H_2O + 2S.$$

Thus, apart from absorption of water from the atmosphere and from reduction of sulphuric acid, 100 grams of the original acid containing :—

77·1	grams	H_2SO_4		77·1	grams H_2SO_4
0·18	,,	N_2O_3		0·05	,, H_2O
0·29	,,	As_2O_3	should give with H_2S	0·08	,, ,,
1·58	,,	As_2O_5		0·63	,, ,,
20·85	,,	H_2O		20·85	,, ,,

i.e. 100 grams of acid should become 98·71 grams after de-arsenication, so that the strength of the sulphuric acid in the de-arsenicated product should be $\frac{100 \times 77{\cdot}1}{98{\cdot}71} = 78{\cdot}1$ per cent. Since it was found to be 77·1, there is an apparent loss of 1·3 per cent. of the sulphuric acid originally present. This figure cannot be taken as accurate, for absorption of water may have occurred, and, further, it is not possible in small experiments to estimate the yield of de-arsenicated acid at all exactly. But it can be taken that the loss of sulphuric acid by reduction is less than 1·3 per cent. of the original sulphuric acid. The loss could certainly be diminished by (*a*) using a more efficient apparatus for mixing the gas with the acid, (*b*) stopping the treatment before the de-arsenication had gone so far as the point reached in the experiment, and (*c*) using a Glover tower acid of more normal arsenic content, for all these conditions would diminish the duration of treatment.

From these experiments it is clear, that for practically complete de-arsenication of acid of any strength up to 95 per cent., the only essential condition is that the acid after treatment must contain dissolved hydrogen sulphide, and so long as this condition is fulfilled, the acid can stand in contact with the arsenious sulphide without any serious increase of arsenic content. As soon as the hydrogen sulphide has been

destroyed, the acid takes up arsenic again at a rate depending upon its strength.

F. Schmidt[1] states that although water, alcohol, and dilute solutions of hydrochloric acid cause appreciable decomposition of arsenious sulphide, this decomposition is prevented by the presence of small quantities of hydrogen sulphide. The above experiments show that hydrogen sulphide has a similar effect, even in the presence of strong sulphuric acid.

There is, of course, greater loss of sulphur in treating, say, Glover acid containing 0·2 per cent. of arsenic, for in this case, the residue emanating from its treatment with sulphuretted hydrogen would probably contain 25 to 30 per cent. of free sulphur, against, under 10 per cent. in the residue from the treatment of weaker acids. Notwithstanding this extra loss of sulphur, at present prices, it would only mean one penny per ton of acid, whereas the saving in concentration costs would be twenty or thirty times this amount.

For the removal of arsenic from strong sulphuric acid the tower system is not at all suitable, and a description is now given of the apparatus which has been proved to give satisfactory results.

The United Alkali Co. (B. P. 126714)[2] heat the acid to about 70°, then treat with sulphuretted hydrogen, and thoroughly agitate with paraffin oil ($\frac{1}{2}$ to $2\frac{1}{2}$ gals. per ton of acid).

The agitating vessel communicates with one end of a horizontal tray, into which the mixture flows.

The scum containing arsenious sulphide separates at the surface, and is mechanically removed by scrapers, which carry it over an inclined shelf at the other end of the tray, and then on to an inclined chute, where it is washed with water. The purified acid leaves the tray through an outlet situated under the inclined shelf; it is filtered if necessary, and run into storage tanks. The scum and wash water are collected and separated, thereby recovering most of the acid, and the scum is treated with an alkaline solution, which dissolves the arsenious sulphide forming a solution of alkali sulph-arsenite, from which the oil separates and is recovered for re-use. The

[1] *Arch. Pharm.*, 1917, **255**, 45.
[2] *J. Soc. Chem. Ind.*, 1919, p. 461A.

sulph-arsenite solution is filtered and utilised as such, or acidified to obtain arsenious sulphide.

In order to more readily treat Glover acid containing a large amount of arsenic, the process is simplified by first removing the bulk of the impurity, by adding hydrochloric acid to the acid, distilling off the chloride of arsenic, and recovering the hydrochloric acid.

The de-arsenicator supplied by Davis Brothers, Barton House, Deansgate, Manchester, is a horizontal washer, similar to those used in gas-works, consisting of several iron rings.

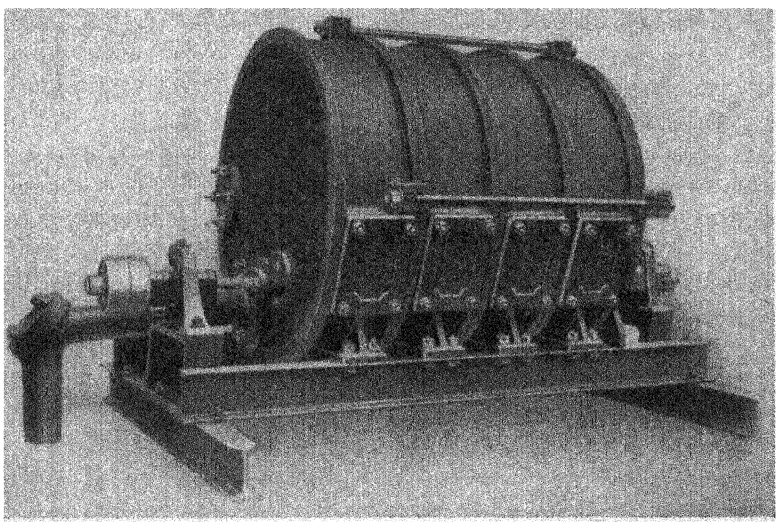

Fig. 163.

Inside these revolves a shaft, provided with agitating-blades, which dip into the acid. The sulphuric acid flows in the opposite direction to the stream of H_2S, by means of overflows through the single compartments. These washers are made in sizes to deal with 20 to 500 tons of acid per week, leaving only 1 to 1½ parts of arsenic in 1,000,000 parts of acid. The plant for dealing with 200 tons weekly covers a ground space of only 6 ft. × 3½ ft.

The apparatus described above is shown in Fig. 163, and is fixed preferably upon an elevated platform commanding the filters, etc. (see B, Fig. 162). This machine is suitable for treatment of all strengths of acid.

Much of the acid sold in England as "brimstone acid" is not made from brimstone, but from spent gas-oxide or from pyrites, and is merely de-arsenicated in the latter case by sulphuretted hydrogen, as described above. Of course, this treatment also removes all nitrogen compounds, lead, selenium, copper, etc., so that this acid, if properly purified, is really purer than real brimstone acid, except, of course, as regards iron. The acid coloured brown by the previous processes (especially where the Gay-Lussac tower has been packed with somewhat soft coke) is rendered much lighter in colour by the precipitation of the arsenious sulphide.

Purification from Nitrogen Oxides.

When dealing with the purification of sulphuric acid from arsenic, it has been stated that most of the nitrogen compounds are removed by the same operation, and this is always the case when sulphuretted hydrogen is employed for that purpose. In most works, however, no such purification from arsenic takes place, and for most uses of the vitriol, the small proportion of nitrogen compounds which it contains is so unimportant that their removal is not called for. In cases, however, where sulphuric acid has to be purified from nitrogen acids, the following methods are available :—

1. *By Sulphur Dioxide.*—Payen has proposed a contrivance for this purpose. This is a cover over the first boiling-down pan, provided with partitions which force the gas to travel twice backwards and forwards, and below which the sulphurous kiln-gas circulates. Some manufacturers, instead of this, use pans arched over. This apparatus, however, fulfils its purpose very inefficiently, because the contact between the acid and the sulphur dioxide is very incomplete. The latter object can be attained perfectly in all works where a Glover tower is employed ; in this the acid can be fully denitrated and, moreover, a small quantity of sulphur dioxide can be dissolved ; but, unfortunately, the Glover-tower acid, owing to its large percentage of iron, cannot well be used for concentration.

At some works, a small preliminary chamber (tambour) is provided in which there are bottom partitions open at opposite ends, so that the acid entering from the next (large) chamber

has to travel a long, circuitous route before it arrives at the place where it is drawn off for use. This is done with the object of completely taking the nitre out of the chamber-acid and making it sulphurous, the fresh burner-gas acting upon this acid with full force. The complete removal of the nitre (and also the selenium) is still better attained by blowing kiln-gases by means of an injector through the acid in a finely divided stream, and allowing the deposit to settle down by running the acid in circuitous channels.

2. *Treatment with brimstone* has been proposed by Barruel. It is used in the form of flowers of sulphur, which sometimes, according to Schwarzenberg, is put into boxes of stoneware placed in the first pan, in which the temperature does not rise to the melting-point of sulphur, and in which the acid contains most water. Special care must be taken that no sulphur gets into the following pans, because strong hot sulphuric acid is decomposed by sulphur with the formation of SO_2, and for each part of S, $6\frac{1}{8}$ parts of SO_4H_2 are lost. According to Bode[1] this process is not efficient; while the brimstone is still in the state of powder its action is very slight, although the lead is already being acted upon by the nitrogen acids. Later, with the rise of temperature, the brimstone melts and rises in small drops to the surface of the hot acid, whence it mostly escapes into the air as SO_2.

3. *Treatment with Organic Substances.—Oxalic acid* has been proposed by Löwe. *Sugar* has been suggested by Wackenroder. Skey recommends agitation with *charcoal*, but only for dilute acid.[2]

4. *Ammonium sulphate* has been proposed for this purpose by Pelouze,[3] and has been proved to be the best of all reagents. By this reagent the nitrogen acids can be so completely removed that the vitriol is tinted red by the first drop of a solution of potassium permanganate. In this case nitrogen escapes, according to the following equations:—

$$N_2O_3 + 2NH_3 = 3H_2O + 4N,$$
$$2SO_5NH + 2NH_3 = 2SO_4H_2 + 2H_2O + 4N,$$
$$3NO_2 + 4NH_3 = 6H_2O + 7N,$$
$$3HNO_3 + 5NH_3 = 9H_2O + 8N.$$

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[1] *Gloverthurm*, p. 3.
[2] *Chem. News*, 14, 217.
[3] *Ann. Chim. Phys.*, 67, 52.

Under normal conditions 0·1 to 0·5 lb. of ammonium sulphate suffices for purifying 100 lb. of vitriol.

It appears as if the addition of ammonia was sometimes carried to a ridiculous excess, for Gintl[1] found, in so-called "chemically pure" sulphuric acid, 5 per cent. of NH_3.

Pattinson[2] recommends the treatment with ammonium sulphate for the sulphuric acid employed for generating carbonic acid in the manufacture of aerated beverages, as an extremely small quantity of nitrous acid (0·026 per cent. of N_2O_3) causes the beverage to be turbid, and destroys the pungency of the ginger essence, etc.

Lunge and Abenius[3] showed that *nitrous acid* (*i.e.* nitroso-sulphuric acid) is very quickly destroyed by boiling with a proportion of ammonium sulphate of 1 NH_3 to 1 acid nitrogen; even with sulphuric acid of 140° Tw. this takes place in five minutes. But *nitric acid* is far more stable. It requires half an hour's boiling with its equivalent of ammonium sulphate, in the case of the strongest sulphuric acid, for its destruction, and many hours' boiling with a large excess of ammonium sulphate in the case of acid of 140° Tw.

K. Rosenstand-Woldike,[4] in order to decolorise acid containing oxides of nitrogen, adds peroxides of lead or barium, which results in the formation of hydrogen peroxide, thus oxidising the nitrogen oxides to nitric acid. The lead or barium formed is precipitated as sulphate, which is insoluble in cold acid. From 0·001-0·01 per cent. of hydrogen peroxide will effectively decolorise ordinary acid, whilst 1·0 per cent. suffices for an acid almost black.

Selenium.

Selenium has been mentioned as frequently occurring in sulphur and pyrites, and hence getting into the acid-chambers, and its presence in the flue-dust and the chamber-mud is well known. In commercial sulphuric acid it has been found, *e.g.*, by Davis[5] and Lunge.[6] It will now be dealt with in detail,

[1] Wagner's *Jahresber.*, 1880, p. 259.
[2] *J. Soc. Chem. Ind.*, 1889, p. 706.
[3] *Z. angew. Chem.*, 1894, p. 609.
[4] *Chem. Zeit.*, 1920, 44, 255.
[5] *J. Soc. Chem. Ind.*, 1883, p. 157.
[6] *Chem. Ind.*, 1883, p. 128.

the main facts being abstracted from a paper by Littmann in *Z. angew. Chem.*, 1906, pp. 1039 *et seq.* and 1081 *et seq.*

Selenium may cause a temporary or a permanent discoloration of sulphuric acid and may also cause other trouble. As is well known, Se is oxidised by nitric acid only as far as SeO_2, and its solutions are reduced by SO_2 to metallic Se. But in the chambers SeO_2 is frequently found where free Se might be expected, and *vice versa*. Free selenium exists in several allotropic modifications, of which the *red* one is of greatest interest here, as it is formed in the reduction of SeO_2 by SO_2 at a moderate heat. It then appears as a brick-red powder, or if present in large quantities, as a voluminous jelly. At temperatures above 80° or 90° it passes over into the metal-like *black-grey* modification, only a very slight proportion remaining in solution, to which it gives a brown colour. It is also known in the *colloidal* state, and as a *green* solution in concentrated sulphuric acid.

Selenic acid, H_2SeO_4, is only formed by the strongest oxidising agents, and is not present in the chambers under normal circumstances. Winteler's assumption to the contrary [1] is erroneous.

The selenium present in the pyrites at first, of course, burns to SeO_2, but the enormous excess of sulphur dioxide, must reduce this to free Se. Yet Littmann always found in the Glover tower, besides free Se, also SeO_2 in varying quantities. The free selenium appears here partly as a dark red sludge, partly dissolved in the Glover acid, to which it imparts a blood-red colour, and from which most of it is precipitated with a light red colour on cooling. Most of the selenium, however, according to Littmann, exists in the Glover acid as SeO_2, owing to the presence of small quantities of nitrous compounds which escape the denitrating action of the tower. This SeO_2 is reduced to free Se by dilution of the acid, and imparts a red colour to it. When employing this red Glover acid on the Gay-Lussac tower, the colour is discharged, all the free Se being converted into SeO_2 by the nitrous compounds. The Glover tower retains at best 20 per cent. of selenium; 80 per cent. or upwards gets into the chambers, and is found there first in the red state of free Se, farther on again as SeO_2. The

[1] *Chem. Zeit.*, 1905, No. 96.

red colour of chamber-acid, due to the presence of free Se, appears in cases where there is too little "nitre" in the chamber, and the Se thus gets into the chamber sludge. The back chambers contain only SeO_2, no free Se, except in cases of extraordinary deficiency of nitre. During the concentration of chamber-acid, which contains both SeO_2 and free Se, the selenium can be partly removed by reducing SeO_2 by an addition of charcoal; but unless it is mechanically removed (which is no easy task), it enters again into solution, and imparts at first a *green* colour to the acid, owing to the formation of the compound $SeSO_3$. When a concentration of 96·5 per cent. H_2SO_4 is exceeded, the green colour vanishes, SeO_2 being reformed. It is hard to say whether the Se causes more damage in the green acid, or in the more highly concentrated colourless acid, from which it is at once precipitated by dilution. The solution of the Se in the form of the green compound begins at 65° and is finished at about 140°; on further heating in the concentrating-apparatus, this compound is again destroyed by oxidation, beginning at 210° and completely at 260° to 280°, and acid so treated contains only colourless SeO_2. The acid distilling over contains no Se in the first and in the last stage of the concentration, but does so in the middle stage. Concentrated sulphuric acid loses its solvent power for Se when it is cautiously and with constant cooling diluted to 84·5 per cent. H_2SO_4; hence the hydrate H_2SO_4,H_2O forms the limit.

Littmann draws the following conclusions:—(1) Under the ordinary conditions ruling in the chambers, all modifications of selenium are oxidised to SeO_2, both wherever there is a formation of nitrososulphuric acid, and wherever the latter is principally decomposed by hydrolysis; an excess of SO_2, if present, has no influence. (2) Most of the Se carried on with the chamber-gases must be in the state of an intermediate, unstable compound, probably SeO, which is easily reduced to Se or oxidised to SeO_2, according to whether the surrounding gas contains an excess of SO_2, or of nitrogen oxides. This compound, if combined with SO_2 or SO_3, is more stable and can exist for some time in chamber-acid, free from SO_5NH, under certain conditions of concentration and temperature. This SeO has never been prepared in a pure state, but it would

explain the presence of selenium in the chamber-gases and in many places where neither Se nor SeO_2 can be expected to exist. Selenium exists in the chamber-acid also in the form of sulphonated compounds, which have been studied by a number of chemists, but without leading to quite certain formulæ. Littmann discusses this matter at length, also the conditions for increasing the production of selenium in the chambers, if demand should arise for it, *e.g.* working with as little nitre as possible. The selenium obtained in the Glover or chamber sludge is advantageously prepared in the following way.[1] The sludge is agitated with concentrated sulphuric acid and as much sodium nitrate as corresponds to the selenium it contains. Water is gradually added, then steam is injected until the acid sinks to sp. gr. 1·26, and the nitrogen oxides still present are driven out by a current of air. A little HCl or NaCl is added to the filtrate and washings, and the Se is precipitated by a current of SO_2 in the form of a red jelly, which is washed with water and dried at 105°. It contains about 99 per cent. Se.

The most usual process for destroying the red colour of sulphuric acid, if due to selenium, is the addition of a little nitric acid, of which, however, any excess is unsuitable for many purposes. Therefore Le Roy[2] prefers to add, at a temperature of 50° or 60°, a sulphuric-acid solution of potassium or sodium permanganate, of which 10 grams at most is required for a ton of acid. The pink colour caused by the excess of permanganate is removed by oxalic acid.

F. Schultz[3] states that petroleum refined with sulphuric acid containing 0·5 per cent. of selenium has a decided yellow tint in comparison with that purified by pure acid. Selenium dioxide has a stronger action than the element itself. The coloration is not removed by subsequent treatment of the petroleum with pure acid. Probably the selenium dioxide acts as a direct oxidising agent, similar to nitric and nitrous anhydride, which have a similar but decidedly greater action than selenium dioxide.

[1] *Z. angew. Chem.*, 1906, p. 1329, Deutsch declares that the process described in the text was not worked out by Littmann, but by himself.

[2] *Monit. Scient.*, 1901, p. 406.

[3] *Chem. Zeit.*, 1911, p. 1129.

The recovery of selenium as a commercial product is described on p. 487, Vol. I, when dealing with the recovery of dust from burner-gas.

Purification by Special Methods (by Electrolysis, etc.).

According to *J. Franklin Institute*, 5, 65, lead, iron, and arsenic can be removed by subjecting the sulphuric acid to electrolysis.

Askenasy (Ger. P. 86977) subjects sulphuric acid for some time to electrolysis and allows the products to act upon the acid. Among these products is ozone, which destroys organic substances and hydrochloric acid (with formation of chlorine); finely divided sulphur, which reduces the nitrogen compounds; and hydrogen sulphide, which acts in the same manner and also in precipitating any metals present. The electrolysis is carried out at ordinary or slightly elevated temperatures, with lead electrodes without diaphragm, and with agitation of the liquid, the agitation being commenced only after the current has acted for some time. The current-density should be 1 or 2 amps. per square decimetre and the tension 6 volts. After a few hours the acid is colourless. It is then heated up, if necessary, in order to agglomerate the precipitate, or else diluted and afterwards filtered.

Nicklès removes *hydrofluoric acid* from sulphuric acid by diluting with twice its volume of water and heating for fifteen hours, replacing the water as it evaporates.

Coloured Acid.

A *brown* colour is so frequently found in sulphuric acid up to about 80 per cent., that the designation "brown oil of vitriol" (B.O.V.) has become universal in England for acid of about 140° Tw. This colour is destroyed during further concentration of the acid, and also by treatment with sulphuretted hydrogen (p. 350), but not always entirely.

Nörrenberg[1] points out that the *red colour* sometimes found in commercial sulphuric acid of about 140° Tw. may be produced by the contact of that acid, when containing a slight

[1] *Chem. Ind.*, 1890, p. 363.

quantity of nitrous acid, with iron tanks. The iron, acting upon the nitrous acid, generates nitric oxide, which is dissolved in the ferrous sulphate formed—thereby producing the red colour. Oxidising agents discharge this colour by converting the ferrous into ferric salt, and the NO into N_2O_3. Completely denitrated acid never assumes the red colour when kept in iron tanks, nor does stronger acid ("rectified oil of vitriol"), which has much less action upon the iron. The same colour may be produced in the small chambers or "tambours" sometimes placed before the first large chamber; here the sulphuric acid is still predominant, and iron is present as flue-dust, so that the conditions are present for the formation of a solution of NO in $FeSO_4$. The main chambers, where nitre predominates, never show that colour, as here all the iron must be present as ferric sulphate.

The red colour frequently imparted to sulphuric acid by selenium has been discussed, *supra*, p. 366.

The colour of waste acid from *nitrating operations* (nitro-glycerine, gun-cotton, nitro-benzene, etc) may also be very strong, but this acid is hardly ever sent into trade. It is usually denitrated at the works where it has been obtained, where the colour remaining in the recovered sulphuric acid is of no consequence. Colourless acid, also free from arsenic and iron, is obtained, according to Girod's B. P. 17157 of 1911, by first purifying the burner-gases mechanically, then passing them, while still hot, over nitrous sulphuric acid, to which a little nitric acid has been added. The nitrous sulphuric acid is afterwards denitrated, any arsenious acid present is oxidised, the gases are passed through washing-towers, and then submitted to the chamber-process.

Preparation of Chemically Pure Acid.

Hayes[1] proposed to add sufficient nitre to sulphuric acid of 152° Tw., coming from the lead pans, to destroy the largest portion of any hydrochloric acid present, and to oxidise completely the sulphurous and arsenious acids, then to destroy the nitrous acid, etc., again by adding $\frac{1}{3}$ per cent. of ammonium sulphate, then to add a little oxide of lead, to allow it to settle

[1] *Dingl. polyt. J.*, 110, 104.

in leaden vessels, and to cool the clear acid siphoned off in shallow lead pans down to $-18°$. In this case the hydrate $SO_4H_2 + H_2O$ crystallises out. The mother liquor containing all impurities is decanted. The crystals are washed with pure acid, and then form square prisms, sometimes an inch thick and $1\frac{1}{4}$ in. long. These are fused in clean lead vessels and used as they are, or further concentrated in a platinum still. This process was intended to save the distillation. It has not been successful, however, for it is troublesome and yet does not produce a really pure acid. Exactly the same plan has been proposed by Tjaden-Möddermann.[1]

The only plan for making perfectly pure sulphuric acid for pharmaceutical and analytical purposes is *fractional distillation*, in conjunction with such operations as previously remove the volatile impurities of the vitriol or convert them into non-volatile compounds. It has been shown (pp. 341 and 361) how the arsenic and the nitrogen compounds can be removed. The latter may be destroyed by ammonium sulphate and the arsenious acid converted into non-volatile arsenic acid, or a little common salt may be added and the first distillate, which contains all the arsenic as $AsCl_3$, rejected. It is safer, on account of the danger of spurting, first to remove both nitrogen compounds and arsenic by means of sulphuretted hydrogen. The acid never becomes absolutely free from arsenic in this way, and it is therefore preferable to employ brimstone acid for rectification.

Pure acid is produced by Verein für Chemische und Metallurgische Produktion, Aussig, Czecho-Slovakia (B. P. 195,960). The gases are drawn from the lead-chamber through a filter to an auxiliary chamber, and then into a tower constructed of incorrodible material containing glass rings, and the uncondensed gases are carried back into the process by means of a fan.

Hydrofluoric acid can be removed as mentioned, *supra*.

The fixed substances, such as iron, lead, copper, etc., remain in the retort on rectifying. In order to avoid contamination with organic substances, the receiver is changed when about one-twentieth part of the acid has come over, and the distillation is interrupted when only one-eighth to one-tenth of the

[1] *Z. anal. Chem*, 1882, p. 218; Fischer's *Jahresber.*, 1882, p. 260.

acid is left behind. The portion distilling between these two limits is quite pure.

The distillation of sulphuric acid in glass retorts is a very disagreeable and even dangerous operation, on account of the strong *bumping* caused by the sudden development of large bubbles of vapour. This is aggravated by the separation of lead sulphate. In such cases, the retort is sometimes lifted up bodily, and of course smashed when it falls back upon its seat. Bumping must therefore be avoided as much as possible, for which purpose the following plans have been proposed.

Berzelius suggests heating the retort more from the sides than from below, by placing a sufficiently wide sheet-iron cylinder upon the grate of the furnace, so that the bottom of the retort just fits into it; the coals in the furnace then only heat its sides. In this case, however, the iron cylinder may act as a cracking ring. A. Müller[1] therefore employs an iron pan, in the bottom of which a special iron ring protects the retort-bottom from heating, whilst the remaining space of the pan, round the retort is filled with fine cast-iron borings. Sometimes the retort is heated in an iron vessel just fitting it, which is generally filled with sand. Reese[2] puts ashes on the bottom, as a bad conductor of heat. Frequently, however, the retort is heated by an open fire, and is merely protected by asbestos or by a paste of clay which is continued up to the curve of the neck, so that the vapour is prevented from condensing too soon.

In any case, the retorts must be made of very good glass, free from knots, equally thick all over, and they must not be too large. The neck must be protected against draughts, and must not extend to the middle of the receiver, as the latter might be cracked by the hot drops of acid falling into it. It is neither necessary nor advisable to cement the joint between the retort and the receiver, or to cool the latter, considering the high boiling-point of the acid; but it is useful to place a strip of asbestos between the neck of the retort and the receiver, in order to protect the latter against over-heating at the point of contact.

Bumping is very commonly avoided by putting in substances which favour a regular evolution of vapour. For this

[1] *Polyt. Centr.*, 1860, p. 1069.
[2] *Dingl. polyt. J.*, 155, 395.

purpose the following substances may be employed:—platinum scrap or wire, for instance in the shape of spirals; bits of quartz, of porcelain, or of very hard coke. Dittmar conducts a continuous slow current of air through the boiling acid for the same purpose.

When distilling about 1 cwt. at a time, it takes from five to six hours of moderately strong heating before the contents of the retort begin to boil. After twelve hours one-twentieth has distilled off. The receiver is now changed; after thirty-six hours (counting from the commencement) the acid is distilled off to within one-eighth or one-tenth, and the operation is stopped. The concentration of the acid depends on the time of the first change of receiver.

The following method is highly recommended, because the danger of handling such large quantities is thereby avoided. A small tubulated retort holding from a pint to a quart is employed. Above this, a little on one side, a bottle of convenient size is mounted, provided with a glass tap, into which the sulphuric acid to be rectified is put, after it has been freed from all volatile impurities by previous heating. The distillation is now started in the small retort, which is about half filled, and into which a few scraps of platinum are put. Afterwards, by means of the glass tap and of a finely drawn-out glass tube, as much acid is allowed to run continuously from the stock-bottle into the retort as is distilling off. The operation may be continued till too large a quantity of fixed substances has accumulated in the retort. This plan is at work, on a small scale, in a few English factories.

Pure sulphuric acid is now obtainable in commerce at such a low price that it could not be produced by any of the means described above. It is in reality manufactured from the weak acid distilling over in the production of rectified oil of vitriol, which is concentrated by evaporation in glass retorts, or preferably in a small platinum still, to the point required.

Schütz[1] again describes this well-known process, without any essential addition of his own.

If acid of 98 per cent. H_2SO_4 is manufactured by concentrating in iron retorts or otherwise, the acid distilling over from the retorts is often of the proper strength of "rectified O.V." (on

[1] *Z. angew. Chem*, 1911, p. 487.

the Continent and in America = 66° Bé.), viz. 93 to 93·5 per cent. H_2SO_4. If the arsenic has previously been removed, the *distilled* O.V. will be practically pure acid.

In England the designation "rectified oil of vitriol" (R.O.V.) or "double oil of vitriol" (D.O.V.) is commonly used, not for distilled sulphuric acid, but for acid concentrated to 93 to 95 per cent. H_2SO_4.

Absolutely pure sulphuric acid is made by Brialle (B. P. 22434 of 1908) by direct oxidation of liquid sulphur dioxide by means of nascent oxygen, obtained by electrolytic decomposition of water. He describes an apparatus adapted to this purpose.

The Thermal Syndicate, Ltd., of Wallsend-on-Tyne, supply retorts made of quartz-glass ("vitreosil") for distilling sulphuric acid in moderate quantities in order to prepare chemically pure acid. They hold 3 to 75 litres; the attached pipes and cooling-worms consist of the same material.

Bressanin [1] prepares absolutely pure sulphuric acid by adding hydriodic acid to sulphuric acid of 50° Bé., filtering through glass-wool or asbestos, and removing the iodine from the filtrate by heating it in vessels of glass free from arsenic.

[1] *Gazz. Chim. Ital.*, **42**, i. 456; *Chem. Centr.*, 1912, **2**, 684.

CHAPTER V

ARRANGEMENT OF A SULPHURIC ACID WORKS ON THE CHAMBER PLAN; YIELDS AND COSTS

ALTHOUGH it is obvious that no fixed rules can be laid down as to the way in which a sulphuric-acid factory should be planned, yet a few remarks upon this subject may be of some use. In the first place, the arrangement of acid-works depends upon whether they are to supply only chamber-acid or acid up to, at most, 150° Tw., or rectified O.V. The first case, which is that of fertiliser-works, and even of some salt-decomposing works, is, of course, the simplest, no concentrating apparatus whatever being required. Formerly such works usually did not possess any, or only small, Gay-Lussac or Glover towers. But although the latter in this case are not called upon to furnish a larger quantity of strong acid than is needed for the Gay-Lussac tower, they do furnish much more than that, and water has sometimes to be used in order to bring the acid down to the strength required; yet it is most irrational, in view of the waste of water, the yield of acid, and even the nuisance produced by noxious vapours, to work without any or without fully efficient Glover and Gay-Lussac towers.

Where acid up to 140° or 150° Tw., but of no special degree of purity, is required (that is, generally in works decomposing salt and for a few other purposes), it is easy to obtain the whole of the acid of that strength without any special concentrating apparatus, by means of Glover towers.

The following remarks refer to the arrangement of the remaining apparatus. The lowest level is always occupied by the pyrites- (or brimstone-) burners; but there must be space left for removal of the cinders. Accordingly, the burners are always erected on the ground-level. The pyrites in large

works arrives on an elevated railway A, Fig. 164, and is tipped into hopper-shaped storage bins C, which command the pyrites breaker D. The ore, upon leaving the breaking and sieving

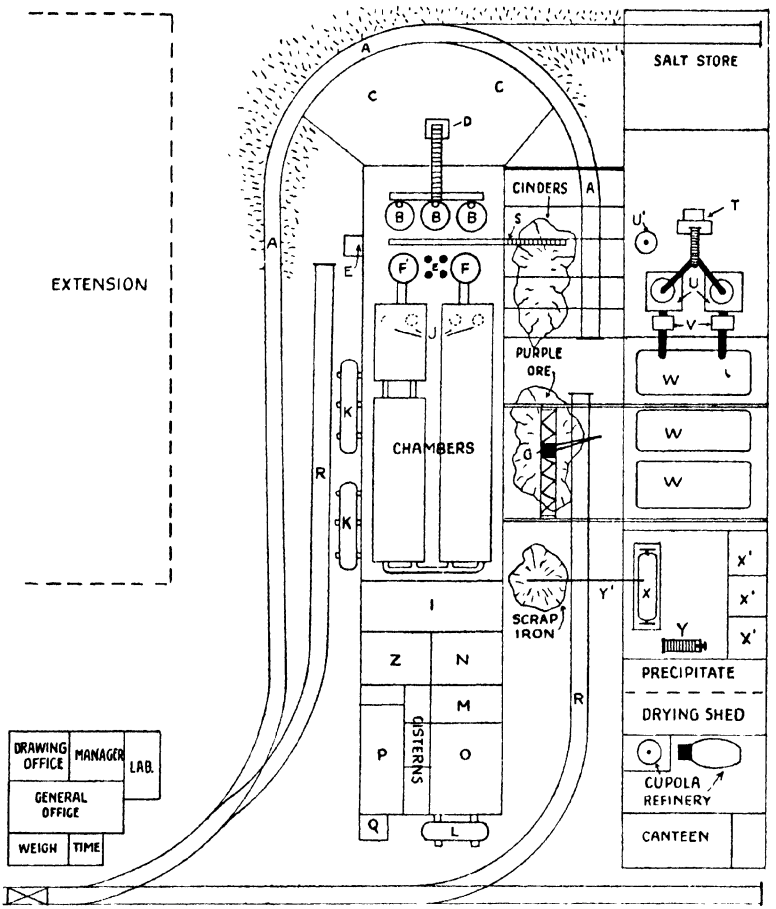

Fig. 164.

A. Elevated Railway.
B. Burners.
C. Pyrites Store.
D. Pyrites Breaker.
E. Ammonia Oxidation.
F. Glover.
F'. Gay-Lussac.
G. Jib Crane (Overhead).
H. Acid Elevators.
I. Plumbers and Fitters.
J. Process Tanks.
K. B.O.V. Stores.
L. R.O.V. Stores.
M. Compressor House.
N. Foreman.
O. Concentration House.
P. De-Arsenication Plant.
Q. Trepex.
R. Low-level Railway.
S. Cinder Elevator.
T. Grinding Mill.
U. Calcination Furnaces.
U'. Gas Producer.
V. Pre-Leacher.
W. Leaching Vats.
X. Precipitator.
Y. Filter Press.
Y'. Scrap-iron Runway.
Z. Stores.

machinery, is transported by any well-known system of conveying to the pyrites-burners B.

In the case of "smalls" ore, the material is only screened.

Unbroken pyrites, especially non-cuprous, can be stored in the open air without much damage, but after breaking, it should be protected from rain. It is sifted directly after, the dust being stored apart from the lumps, and both are taken to the burners across a weighing-machine. The breaking, sifting, and storing of the broken pyrites sometimes takes place underneath the chambers. Where these are high enough above the ground, the burners themselves can be placed beneath them. Otherwise they are erected in a separate shed immediately adjoining, and it is advisable to take this course in all cases. Any cooling-pipes or connections are arranged along the side or on the top of the chambers. Where the burners are built under the chambers, the outer pillars of these must be connected by a light open-work wall, to keep the wind off the burners.

When nitre-ovens are provided, they are always built at the end of each set of burners and as a continuation of it.

In the case of ammonia oxidation units, the apparatus is erected preferably in a house to itself, E, for it is essential that every precaution should be taken to prevent dust getting on the catalyst.

Steam generation plants are not always provided. The more modern works are now generally equipped with electric motors operated by current supplied by the local authority, or the machinery is driven by gas-engines.

In the event, however, of either a gas-engine or a steam-boiler being decided upon, it is not advisable to instal these under the chambers owing to the liability of accidental leakage of acid, and secondly on account of the vibration of the machinery.

The Glover tower must be placed between the burners and the chambers. Formerly, a few burners were sometimes set aside for working the nitre-ovens, the nitre-gas being taken direct into the first chambers; this is very rarely done now, but each set of burners is followed by the nitre-ovens and then by the Glover tower. Where liquid nitric acid or the ammonia oxidation process is employed, the nitre-oven is simply omitted. The Glover tower must be placed with its base rather higher than the top of the gas-flue over the

burners. In this way the burner-gas can travel horizontally to the tower. The flue, however, is generally made a little higher and inclined slightly into the tower, so that any acid splashing into the pipe runs back into the tower. Usually the levels of the Glover tower and the chamber are planned in such a way that the gas issuing from the tower can still enter the chamber below its top. This secures good draught into the chambers, provided there is a sufficiently strong pull at the exit-end.

In all up-to-date factories, it is now usual to provide fans to give the necessary draught.

The chambers, as already mentioned, are either arranged so that their floors are all at the same level, or so that each following chamber is from 1 to 3 in. higher than the preceding one. A greater difference is not necessary, but is sometimes employed for local reasons. A pipe connects the last chamber with the Gay-Lussac tower; it is preferable to have this pipe rising to the tower.

In any case, the Gay-Lussac and Glover towers should be combined into a set, with the necessary tanks and elevators arranged at the foot, by which the attendance will be much facilitated. In large works with several sets of chambers, it is preferable to combine several Glover towers, and in any case, several Gay-Lussac towers, to form a set.

In choosing the site for a works in the tropics, it is advisable to carefully consider the question of the drainage. In any case, the floor should be well above the known flood level, and pits or cellars avoided if at all possible.

The chambers should be protected against the intense heat and heavy rains. For instance, the monsoon of western India will continue for two to three months, and upwards of 90 in. of rain will fall in that period. Plenty of room should be left between the chambers in order to allow for cooling and to give space for the workers to supervise or repair the plant.

The area devoted to lighting in the roofs should be kept as small as possible, as the intense heat and light are detrimental to those in charge.

In designing an acid plant for these warmer climates, it must be borne in mind that a greater allowance of chamber-space must be given, and at least 12 cub. ft. per lb. of sulphur

per twenty-four hours be arranged for, where pyrites is the material to be used.

In Lunge's fourth edition, p. 1230 *et seq.*, full details and drawings are given of a plant designed by Niedenführ, which has a capacity of 20 tons of O.V. per twenty-four hours, in the form of chamber-acid. The chamber-space is stated to be equal to 19 cub. ft. per lb. of sulphur per twenty-four hours.

It consists of three chambers of equal size, one Glover tower square in section, and two circular Gay-Lussacs, the various sizes being as follows:—Glover, 29·5 ft. high by 9·8 ft. sq.; Gay-Lussacs, 46 ft. high by 9·8 diam.; three chambers, each 112 ft. × 26¼ ft. × 31 ft. wide. The Glover was packed with bricks on edge half-way up, the remainder with dishes. The Gay-Lussac was packed with dishes and the other with coke, the capacity of the two being equal to 2½ per cent. of the chamber-space.

With regard to the cost of erecting an acid plant, it is futile to give an estimate at this period (1923). The futility of doing so will be readily appreciated when the following facts are considered.

In Lunge's fourth edition, page 1233, the cost of a certain plant for the production of 20 tons of O.V. per twenty-four hours, in the form of a chamber-plant, is given as £14,500, whereas, owing to the increased cost of material and labour brought about by the great European war, the cost of a similar plant in, say 1921, would be approximately £40,000, exclusive of the cost of the steam installation. About the middle of 1923 the cost would not have exceeded £25,000.

Fig. 165 gives a sketch of a set of chambers designed by H. H. Niedenführ, as embodying the *later progress in the combination of chambers and towers*. This set is to suffice for burning 20 tons of 48 to 50 per cent. pyrites in twenty-four hours. The pyrites is burned in Herreshoff furnaces *a*, *a* (*cf.* Vol. I, p. 377), or in any other kind of pyrites-kiln or burner. The gases first pass through the dust-chamber *b*, *b*, then through the Glover tower *c*, into the lead-chamber *d*, provided with air-cooling shafts (p. 55) and water-spray injectors (p. 109 *et seq.*). From here they pass through plate-tower *e*, containing 10 layers of 28 plates each, at a distance of 12 in. from layer to layer, then into another lead-chamber *f*, followed by plate-tower *g*, with 10

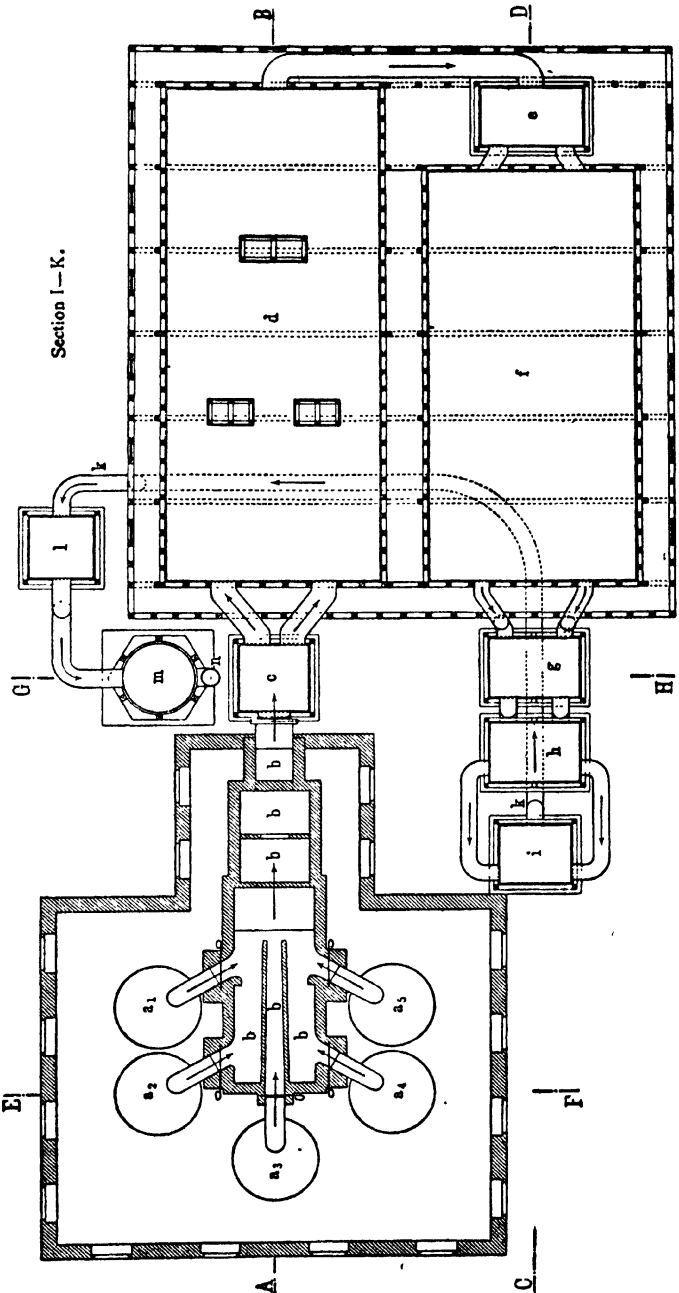

FIG. 165.

layers of 24 plates each, 12 in. apart, and plate-tower *h*, with 12½ layers of 24 plates 12 in. apart; finally at the top into plate-tower *i*, containing 16 layers of 20 plates each, 8 in. distant. They leave this tower at the bottom by the long conduit *k*, which takes them to the first Gay-Lussac tower *l*, containing 24 layers of 16 plates each, 4 in. distant; and this is followed by the coke Gay-Lussac tower *m*, a fan being placed between these two towers.

Niedenführ calculates the work to be done by this set as follows :—

		H_2SO_4 kg.
Chamber *d*	= 1819 cub. met. at 4 kg. H_2SO_4	= 7,276
Plate-tower *e*	= 280 plates ,, 12½ ,,	= 3,500
Chamber *f*	= 1516 cub. met. ,, 2 ,,	= 3,032
Plate-tower *g*	= 240 plates ,, 8 ,,	= 1,920
,, *h*	= 288 ,, ,, 4½ ,,	= 1,296
,, *i*	= 320 ,, ,, 2 ,,	= 640
Production of Gay-Lussac and Glover towers		= 2,336
		20,000

Interesting notes are contained in the papers of Falding[1] and of Gilchrist[2] on the arrangement of sulphuric-acid works in the United States.

YIELDS AND COSTS OF SULPHURIC ACID MANUFACTURE.

In calculating the cost of manufacturing sulphuric acid, the following factors must be taken into account :—

Raw materials (pyrites, brimstone, etc.).
Nitre.
Power, fuel, etc.
Wages.
Repairs.
General.
Interest and depreciation.
Yields.

The first point to consider is the *consumption of nitre* and the *yield*. At the outset the difficulty arises of comparing the

[1] *Min. Ind.*, 8, 579, and 9, 617.
[2] *J. Soc. Chem. Ind.*, 1890, p. 459.

statements from different sources, arising from different fundamental quantities being taken as the basis of the calculation. Some calculate all the sulphur contained in the charge, others only that portion which has actually been burnt, not taking into account the sulphur left in the cinders. The latter way of calculating is more rational in theory; but in practice it is often less useful than the former. For it is known with perfect accuracy, how much pyrites, and how much sulphur contained in it, has been put into the burners, but as the percentage of sulphur in the cinders varies, it is not known precisely how much has been burnt. Besides, the question is not only how the chamber-process itself works, but also how the burning has been done, on which the smaller or larger residue of sulphur in the cinders depends. It is entirely different when the percentage of sulphur in the cinders is almost constant and very slight, as in burning pure ores in shelf-burners. In this case, it is immaterial which way is adopted of stating the results.

The *consumption of nitre* is stated sometimes in percentages of pure sodium nitrate, sometimes in percentages of commercial nitrate, and in the latter case either 95, 96, or 97 per cent. is assumed. Here also there is a source of uncertainty and divergence, although not of such importance as that just mentioned.

The worst confusion prevails regarding the calculation of the *yield of sulphuric acid.* Some state it in terms of chamber-acid of 50° Bé. (= 106° Tw.), some as 60° Bé. (= 144° Tw.), some as commercial 168° Tw. (= 66° Bé.), some as real monohydrate. Worse still, the reduction to these terms is made by very varying and, in part, quite erroneous tables (*cf.* p. 202 of Vol. I), and frequently it is quite uncertain whether by "oil of vitriol" (O.V.) an acid of 93 to 94, or one of 96 to 98, or one of 100 per cent. H_2SO_4, is meant. In the following pages, so far as the sources permit, all statements will be reduced to the only rational term, that of monohydrate, H_2SO_4.

Frequently, at works where none of the sulphuric acid is sold, but the whole is used for making salt-cake, the yield is calculated indirectly, from the quantity of common salt decomposed by it, according to more or less arbitrary assumptions regarding the quantity of sulphuric acid consumed for decomposing a unit of salt.

Often it is not mentioned whether that portion of the sulphuric acid employed for the *decomposition of nitre*, which leaves the factory in the shape of acid sulphate (nitre-cake), has been allowed for in the calculation. This is specified in the following accounts, wherever it can be done from the sources.

Of course, the following enumeration does not contain all and every statement of the kind scattered in innumerable publications, but only so much as suffices for forming a good idea of the state of affairs, both in former and in recent times.

I. Consumption of Nitre.

According to Lunge, fourth edition, p. 1238 *et seq.*, the consumption of nitre in 1866, at works burning sulphur, without recovery by the Gay-Lussac, was between 10 and 6 parts per 100 parts of sulphur charged.

With recovery of nitre the consumption was 5 parts down to 3 (in 1890).

For pyrites acid without recovery, the figures were 14·4, down to 6·5 parts per 100 parts of sulphur more recently; with nitre recovery, 5·8 parts in 1877, down to 2·3 parts in more recent times.

Since Lunge's last edition, much lower amounts have been used, and for long periods, namely, 1·6 parts of nitre per 100 parts sulphur.

The consumption of nitre is generally less in winter than in summer. The difference between the use of nitric acid and solid nitre is negligible; if anything, slightly less nitre is used in the solid form than as nitric acid. If nitric acid is used, the nitre from which it was originally made, should be taken as the basis of calculation.

II. Yield of Acid, calculated as H_2SO_4.

(Theoretically 305·91 parts per 100 sulphur.)

1st. *From brimstone* (always upon the sulphur actually burnt) 290 to 300, on the average 296 (Knapp); 297 $H_2SO_4 = 319·35$ acid of 66° Bé. (Schwarzenberg); "usually 296 to 300; even the theoretical quantity has been obtained" (*sic!* Payen, 1, 321); 290 to 300 (Scheurer-Kestner).

2nd. *From pyrites.* At Oker, in 1857, 1 cwt. acid of 66° Bé. per 1·89 cwt. ore (Knapp); 1859-1863, 1 cwt. acid of 66° Bé. per 1·729 cwt. ore (Kerl-Stohmann); 1877, at the same place, 160 chamber-acid of 50° Bé. (106° Tw.) were obtained from 100 pyrites; from 100 rich copper-ores 140 to 150 parts of chamber-acid, from 100 "mixed-ores" 90, from 100 ore mixed with galena 70 parts of chamber-acid. The residual sulphur in the cinders from pyrites (always containing galena) amounts to 6 per cent.; from the other ores, 10 to 12 per cent. (Bräuning).

In four Belgian works, 1854 (*Official Report*), on 100 parts sulphur in the pyrites charged 242, 237, 259, 238 parts H_2SO_4. The same works in 1874 by improved arrangement had arrived at 87·81, 92·17, 85·50, 89·30 per cent. of the theoretical quantity, or 268·8, 282·4, 261·8, 273·5 H_2SO_4 per 100 S (Chandelon).

In the best French works (Schwarzenberg), on 100 parts sulphur in the pyrites charged, 259·7 H_2SO_4; on the sulphur really burnt 283·43. Payen (*loc. cit.* p. 322) makes precisely the same statement, with the addition that *usually* from 100 kg. 46 per cent. pyrites 100 to 115 kg. acid are obtained (= 239·1 to 250 H_2SO_4 per 100 sulphur). According to Scheurer-Kestner (*loc. cit.*) there ought to be the same yield on the sulphur of pyrites really burnt as upon brimstone, viz. 290 to 300 parts. According to Wright, with rich Spanish pyrites 82 to 84 per cent. of the sulphur is obtained as acid; of the loss of 16 to 18 per cent., 4 or 5 per cent. is sulphur left in the cinders, and 12 or 14 per cent. other losses. This means a yield of 251 to 257·25 parts H_2SO_4 per 100 parts sulphur charged (evidently with insufficient chamber-space). An anonymous chemist (in the *Chem. News*, xiv. p. 22) states the yield from 30 per cent. Irish pyrites as 82 to 81·1 per cent. of the theoretical, inclusive of the sulphur in the cinders.

The writer considers that working with cuprous pyrites, where usually it is the custom to leave 4 to 5 per cent. of the sulphur in the cinders, a yield of 280 parts of acid is quite satisfactory.

Cause of the Losses in Manufacturing.

The causes of the *loss of nitre* have been mentioned in detail, p. 317 *et seq.* They are (1) loss of nitre-gas carried into the outer air; (2) nitrogen compounds left in the chamber-acid; (3) nitre-gas reduced to N_2O or N.

The *loss of sulphuric acid itself* arises from the following causes:—

1. Incomplete combustion of the sulphur (loss in the cinders); this has also been considered before (p. 326 *et seq.* of Vol. I). With brimstone, this loss is very slight; with pyrites it is so much the greater the poorer the ores, and it also varies enormously according to the construction of the burners and the care with which they are worked, being from 1 to 10 parts and more of sulphur per 100 parts pyrites, or from 2 to 30 per cent. of the total sulphur. A portion of the sulphur is sublimed, and is found in the connecting-pipes and in the acid itself, and is a clear loss.

2. Losses of SO_2 by leakages of burners, pipes, chambers, etc. A heavy loss may be caused by bad draught, as the gas continually blows outwards at the doors of the burners, nitre-ovens, etc. Bad pipe-joints, and especially chambers out of repair, lead to great losses. Many manufacturers have no idea of the great loss which they suffer in this way, by allowing, from motives of ill-timed economy, a chamber to go on too long and trying to patch it up. Wright found in a chamber-system that went three years without repairs:—

	Nitre for 100 parts of sulphur burnt.	Cub. ft. of chamber-space per lb. of sulphur burnt per 24 hours.	Practical yield (theoretical = 100).
First year . .	9·31	13·0	81·5
Second year . .	9·84	14·5	75·4
Third year . .	10·02	15·0	68·4

3. Losses of SO_2 by *incomplete conversion into sulphuric acid.* Extremely little SO_2 can remain dissolved in chamber-acid if there is an excess of nitrous compounds present. The greater portion of any remaining SO_2 escapes from the chambers into the outer air. The reason of this may be irregularity of the process in general, want of nitre, insufficient chamber-space,

insufficient draught, etc., as explained in detail previously. The losses from this source are nearly always much greater where the nitre is not recovered, for the reasons stated above. The very widely divergent statements respecting the yield of sulphuric acid are explained to a great extent from this cause alone.

An apparatus for indicating the loss of acid by leakage in various parts of an acid-works is described by Hideo Utsunomiya and Junichi Kamiryo, in Jap. P. No. 40620. A lead pipe is attached to any piece of plant from which acid is likely to leak, which delivers the leaking acid to an electrolytic cell containing water and connected in circuit with a warning bell or lamp.

III. Costs.

The Committee appointed by the Minister of Munitions in February 1917 report upon the cost of production of sulphuric acid as follows :—

"(1) That for high-strength acid, such as is employed in the dye industry, explosives manufacture, and in a few other small trades, the contact system is the cheapest and most efficient.

"(2) That for low-strength acid, such as is usually employed in the manufacture of fertilisers, there is little to choose between the Grillo contact system and the ordinary chamber-plant as regards cost of production as SO_3, but other factors must be brought into reckoning, such as reduction of strength, storage facilities, and factory room, which are to the advantage of the chamber-system. It seems obvious that when burning pyrites or zinc concentrates, the Grillo plant could only be successfully run in competition with the chamber-plant for low-strength acids if the plant were run continuously at a high standard of efficiency.

"(3) The cost of production cannot be dissociated from the question of the locality of the acid-works, since ultimately it is the cost of acid delivered that counts ; the close proximity of the acid-works to the consuming factory is one of the most important factors in determining its ability to compete. This is a point of fundamental importance, and the estimation of the relative efficiency of different factories in terms of the actual

cost of production at these factories without having regard to their locality, is liable to be highly misleading. The real importance of the cost of any commodity is the cost to the consumer at the point of consumption and not at the producers' works. It is seldom possible for an acid works badly situated, or built on too large a scale, to be able to make up by efficiency of working for the extra carriage involved in distributing the acid produced.

"(4) That although the majority of manufacturing trades are dependent on supplies of sulphuric acid, in relatively few of these is the cost of acid an important factor, since the charge for acid in relation to the total cost of the manufactured goods is often very small or negligible. This applies to the whole group of engineering trades, to the textile trades, to leather, paint, and several smaller industries. In the case of the manufacture of artificial fertilisers the charge for acid is a relatively large proportion of the total cost of production, and in the manufacture of superphosphates, where competition is keen, the cost of acid is a factor of supreme importance. Whilst, therefore, efficient working and low cost of production are considered essential throughout the industry, it becomes a manufacturing problem of even greater importance when associated with the production of superphosphate.

"(5) That, in spite of the fact that some acid works have in the past paid much attention to the question of costs, and have succeeded in producing acid at a low figure, there can be no doubt that the scientific study of costs has not been the uniform practice of the trade as a whole. This is a criticism applicable to other industries as well as the acid trade, but it is nevertheless impossible to state too strongly the need and importance, both in the interests of consumers as well as of producers, of a profound change in the methods of cost-keeping, and of the application of strictly scientific methods to the study of costs in every operation of manufacture.

"A system of cost-keeping and of close study of costs was developed in great detail at the Government factories. Very extensive records from month to month have been kept, not only in connection with the acid plants but with each operation in the manufacture of explosives.

"It would be of great advantage if the information thus

collected could, as far as possible, be placed at the disposal of private manufacturers, not only on account of its intrinsic value, but as an illustration of a method of work which is only too little followed in this country."

From Pyrites.

The following was the cost per ton of 140° Tw. acid early in 1922 in a plant producing 20 tons per day, using the ordinary chamber-system.

The cost of de-arsenication and concentration is excluded; interest and depreciation are taken on the present cost of the plant:—

	s.	*d.*
Raw material—		
Pyrites at 8d. per unit, 94½ per cent. efficiency	17	5
Carriage and cartage		2
Nitrate of soda at £16 per ton, at 1·0 per cent. on O.V. made	2	5½
Repairs—Material	2	3
Power—		
Fuel		2
Water		8½
Electric		11
Wages—		
Crushing	1	1
Process	4	4
General	2	3
Repairs (plumbers and labourers)	3	0
Establishment charges—Rates, taxes, rents, etc.	7	2
Depreciation, 10 per cent. on £25,000	7	1½
Interest on capital, 6 per cent. on £25,000	4	3½
Total	53	4

The cost of sulphur will have to be modified (1) if the works can burn pyrites from their own mines; (2) if pyrites containing copper is treated and the yield of copper credited to the acid process; (3) if spent oxide of gas works is utilised; (4) if burner-gases from zinc works can be purchased favourably; and (5) if sulphur is used.

From what has been said above relative to the competitive costs of producing acid by the contact and chamber-processes, manufacturers using the latter system ought to maintain their plants in the fullest state of efficiency by employing all rational improvements, and the use of well-built furnaces, efficient packing material for the various towers, and expeditious handling of all materials.

CHAPTER VI

OTHER PROCESSES FOR MANUFACTURING SULPHURIC ACID

ALL other processes which have been proposed for producing sulphuric acid, numerous as they are, can be dismissed with a few words, since many of them have not had any technical success or have afforded no prospect of becoming successful. The details can be found in the places quoted.

I. PROCESSES DISPENSING WITH NITRE

Deacon showed in 1871 [1] that a mixture of SO_2 and atmospheric air in the presence of a solution of cupric sulphate is converted into sulphuric acid, but this does not seem to have become widely known. Later, the same invention was made by Roessler, and was specially applied to the absorption of acid smoke. It is hardly applicable to the manufacture of sulphuric acid proper, but possibly to that of copper sulphate from waste sulphur dioxide. The same process, extended also to salts of manganese, iron, or tin, has been patented by Clark (for Dagiun), 3669 of 1888.

Sébillot (Ger. P. 109484) passes SO_2 and air through towers packed with pumice, into which steam and more air are passed. The temperature is kept below the boiling-point of sulphuric acid, and no nitric acid is used.

Bender (Ger. P. 195810) subjects a mixture of SO_2 and O, with or without N, to the action of the oxy-hydrogen flame, *e.g.* by heating water in a furnace like a gas-producer up to the point of decomposition, burning sulphur at the same time and exposing the SO_2 formed in the presence of an excess of

[1] *Chem. Trade J.*, 1889, 5, 193.

oxygen or air to the action of the oxy-hydrogen flame. The latter furnishes both the heat necessary for the process and the water required for the formation of H_2SO_4. The presence of nitrogen is useful for this process. In this way, about 90 per cent. of the theoretically possible quantity of sulphuric acid is obtained (Fr. P. 377442; U.S. P. 900688).

Kühne (B. P. 17520 of 1908; Ger. P. 203541; Fr. P. 393461) exposes sulphurous fumes purified from flue-dust, and mixed with air and water or steam, to the action of a source of light, rich in ultra-violet rays, such as a mercury vapour lamp, enclosed in a quartz globe. The SO_2 is thus almost completely converted into H_2SO_4, even when only 1 per cent. is present in the air. Aqueous solutions of SO_2, mixed with air, may be treated in the same manner.

Coehn and Becker (Ger. P. 217722) cause the combination of SO_2 and O by exposing the mixture to ultra-violet light-rays at temperatures above 300°. The mercury lamps employed for generating these rays must not be constructed on the lines most suitable for illuminating purposes, but they must work with low mercury vapour pressures, which at higher temperatures allow of attaining a very rapid chemical action. (The application of ultra-violet light for oxidising SO_2 is already mentioned in B. P. 10881 of 1904; it is at present only of scientific interest.)

Hallock (U.S. P. 930471) subjects SO_2 to the influence of an ionising agent, *e.g.* radio-active material in the presence of oxygen; SO_3 is thereby produced.

By Electricity.

Reynoso, in 1875, obtained a patent for causing electric sparks to pass through a compressed and cooled mixture of sulphurous acid and atmospheric air. The formation of SO_3 from a mixture of 2 vol. SO_2 and 1 vol. O by the electric spark was first observed in 1860 by H. Buff and A. W. Hofmann.[1] Deville[2] has observed that in the presence of strong sulphuric acid, which absorbs the SO_3, the whole gaseous mixture can be united to form SO_3 in this way.

Wacker (Ger. Ps. Appl. W10532 of 1894 and 10591 of

[1] *Ann. Chem. Pharm.*, 113, 129. [2] *Bull. Soc. Chem.* (2), 3, 366.

1895) proposes to prepare concentrated sulphuric acid by electrolysing water or dilute sulphuric acid through which a continuous stream of SO_2 is being passed. He employs an earthenware vessel, divided into two cells by a porous earthenware diaphragm. Into the anode cell a slow stream of SO_2 is introduced. In the cathode cell a magma of sulphur is formed, very little H_2S being given off. If hydrochloric acid is added, no sulphur is separated, the chlorine formed by electrolysis directly oxidising the SO_2. Other oxygen carriers may also be employed, such as sodium chloride or sodium sulphate, which acts by forming persulphuric acid; or else chlorates, nitrates, and so forth. (This process, in its present form, is a very peculiar one.) *Cf.* also Van Denberg's patent, *infra*, p. 394.

C. B. Jacobs (U.S. P. 704831 of 15th July 1902) forces SO_2 through a porous anode, and oxidises it by the oxygen of water decomposed at the anode. The SO_2 is oxidised in the lower region of the bath, and the oxidation product is retained remote from the cathode. A sufficient current-density is maintained at the cathode to prevent the access of SO_2 to it and to cause the rapid escape of hydrogen. The inventor claims[1] to attain an electrolytic efficiency of 54 per cent. with a potential difference of 2 volts and a current density of 15 to 20 amperes per square foot of anode surface.

A process for the electrolytic preparation of sulphuric acid is described in A. Friedländer's Ger. P. 127985. Dilute sulphuric acid or water is electrolysed with application of diaphragms, and sulphur dioxide is passed into the anode cells during electrolysis. The anode cells are separated from the cathode cells in such a manner that the gaseous contents cannot mix. The contents are kept under the requisite pressure, and the heat of reaction is conducted away by internal or external cooling. In the cells the reaction is $H_2SO_4 = 2H' + SO_4''$. The hydrogen is discharged at the cathode and is conducted away. The SO_4'' ions migrate through the diaphragm to the anode, where they find SO_2 and react with it thus: $SO_4 + SO_2 = 2SO_3$. The liquids remain perfectly clear, and there is no separation of sulphur as in previous attempts at the electrolytic preparation of sulphuric acid from SO_2.

Boehringer and Söhne (Ger. P. 117129) attain the same

[1] *Min. Ind.*, 10, 602.

object by adding manganous sulphate to the sulphuric acid in the anode cell. The sulphate serves as an oxygen carrier and thus converts SO_2 into sulphuric acid, ultimately up to sp. gr. 1·78.

Salom (U.S. P. 755247) oxidises SO_2 in contact with water by electricity in a number of superposed vessels, each of which constitutes an electrolytic cell.

Johnson (U.S. P. 825057) saturates 20 per cent. sulphuric acid with SO_2 and submits this solution to electrolysis, using lead electrodes; the cathode receives a copper covering. The result is sulphuric acid of 30 per cent. A portion of the acid is now withdrawn, the remainder is diluted, saturated with SO_2, and the electrolysis repeated.

Basset (B. P. 21475 of 1907; Fr. P. 370170) describes a cell in which a solution of SO_2 in dilute H_2SO_4 is one electrolyte, and a solution of N_2O_4 in dilute sulphuric acid the other electrolyte. The reaction is: $SO_2 + NO_2 + H_2O = H_2SO_4 + NO$. The NO is oxidised into NO_2 outside the cell.

Fischer and Delmarcel [1] describe experiments on the electrolytic oxidation of SO_2 in aqueous solutions.

Briaille (B. P. 22434 of 1908; Fr. P. 393665; U.S. P. 928864) describes an apparatus for obtaining sulphuric acid from SO_2, at the same time concentrating and purifying it, by the electric current.

Garroway (B. P. 1755 of 1903) passes purified pyrites-burner gases into towers, together with air previously ozonised by alternating-current electricity of high intensity and containing nitrogen oxides.

Riesenfeld (Ger. P. 229274) obtains an almost quantitative oxidation of SO_2 to SO_3 by the action of electric sparks on roaster gases, or other mixtures containing SO_2 and O, keeping the temperature during the whole process, or at least towards the end, below 46°. At such temperatures the reaction of ozone is not $SO_2 + O_3 = SO_3 + O_2$, but $3SO_2 + O_3 = 3SO_3$. Air alone may be sent through an ozoniser and made to react with SO_2 below 46°.

Kee jun. and Wedge (U.S. P. 1220752) mix sulphur dioxide and oxygen and expose them to an electrical discharge after leaving the Glover tower and before entering the

[1] *J. Soc. Chem. Ind.*, 1910, p. 694.

lead-chamber, or at any other points between the Glover and Gay-Lussac towers. By cooling the nitrogen oxides from the temperature of the electric arc to a temperature suitable for their absorption by sulphuric acid, their reversion to nitrogen and oxygen is prevented.

Bradley (U.S. P. 1284176) passes the burner-gases, after being freed from dust in an electrical precipitator maintained at a sufficiently high temperature to avoid deposition of sulphuric acid, through a Glover tower in which partial oxidation of the sulphur dioxide is said to be effected; they are then cooled to form sulphuric acid mist, which is removed in a second electrical precipitator. The statement regarding oxidation of the sulphur dioxide in the tower appears to require confirmation.

H. V. Welch (U.S. P. 1284166 of 1918; *J. Soc. Chem. Ind.*, 1919, p. 73) mixes sulphur dioxide, oxygen, oxides of nitrogen, and water in the form of gases containing non-gaseous particles; the reactions are then accelerated by producing agglomeration and precipitation of liquid particles by the successive action of electrical fields of sufficient intensity. Oxides of nitrogen and fumes of sulphuric and nitrosyl-sulphuric acids are recovered from the effluent of the chamber-process by passing the waste gases through a chamber fitted with electrodes, between which a high potential difference is maintained. The electric discharge produced precipitates the fumes on the collecting electrodes, from which they are recovered by washing the electrodes with concentrated sulphuric acid.

Weber (U.S. P. 1291306) passes the air going to the burners through flame arcs or through a Kilburn Scott three-phase alternating current electric furnace in order to produce the oxides of nitrogen required.

Alternatively, the air containing sulphur dioxide may be treated as it leaves the burners, or if the content of sulphur dioxide is high, a suitable quantity of air containing oxides of nitrogen may be added at a point between the burners and the fan.

II. From Sulphates.

The neutral sulphates of the alkalies, the alkaline earths, and lead are practically unchangeable at a red-heat. The acid (primary) sulphates of the alkalies are first changed into pyrosulphates ($2NaHSO_4 = Na_2S_2O_7 + H_2O$), and the latter afterwards split up into neutral sulphates and sulphuric anhydride. This reaction, for obvious reasons, cannot be thought of for the manufacture of sulphuric acid proper, but only for that of fuming acid.

Most of the other sulphates are no better adapted for the manufacture of sulphuric acid. Only those of very slightly positive metallic radicals, more particularly ferric oxide and alumina, and the acid sulphates of other radicals, yield up their sulphuric acid at a comparatively low temperature, and consequently all or the greater part of it undecomposed. The other sulphates split up at a much higher temperature, mostly decomposing into metallic oxides, sulphur dioxide, and oxygen, and yielding only a small portion of their sulphuric acid as such or as anhydride. Even if it were otherwise, their high price would make their employment for the manufacture of sulphuric acid impossible. Most of them are themselves produced by means of sulphuric acid made in the ordinary way. From even the cheapest and most easily decomposable of all the sulphates in question, ferric sulphate, only fuming oil of vitriol can be made, and that only under especially favourable circumstances.

Goldmann[1] mixes galena with about 20 per cent. of limestone, and then subjects the mixture to a preliminary sintering in a cylindrical coke-fired furnace, the sole of which has a diameter about 24 ft. and revolves at a speed of 20 revs. per hour.

The mixture, which contains 11 per cent. of sulphur, loses in this way 10 per cent. of its sulphur content, the furnace gas containing 0·15–0·20 per cent. of sulphur dioxide. After roasting in a special furnace, a gas containing 4-5 per cent. sulphur dioxide is obtained.

From Calcium Sulphate.—The enormous quantities of sulphuric acid occurring in nature in gypsum or anhydrite, and

[1] *Metall und Erz*, 1919, 16, 41-48.

nearly worthless in this form, have occasioned many proposals for their technical utilisation.

Kuenzi[1] fluxes gypsum with quartz, sand, clay, etc., to an easily fusible slag, whilst SO_2 and O escape. The same proposal was made by Frémy and also by Archereau,[2] by the latter for the purpose of utilising the oxygen as well.

O. Schott[3] ignites sodium sulphate, gypsum, and coal in order to obtain a frit for glass-making. The SO_2 is to be conveyed into a lead-chamber along with the other gas and converted into sulphuric acid.

Martin[4] describes making an artificial sulphide by smelting 1700 parts of gypsum, 1000 of ferric oxide, and 500 of coal in a blast-furnace. This sulphide is to be burnt like natural sulphides. In this case at most a monosulphide of iron will be obtained, and that will cost more than the best pyrites.

Scheurer-Kestner asserts that calcium or magnesium sulphate, when calcined with ferric oxide, preferably with addition of fluorspar, gives off sulphuric anhydride.

Cummings (U.S. P. 342785; B. P. by Lake, 7355 of 1886) calcines a mixture of gypsum and clay in a suitable kiln. A hydraulic cement is formed, whilst SO_3, SO_2, and O are expelled, and are converted into sulphuric acid in the usual manner.

Van Denberg (U.S. P. 642390) electrolyses calcium sulphate in a furnace in a molten condition in the presence of an excess of oxygen, thereby forming SO_3, which is subsequently hydrated.

Anzies (Fr. P. 420675) calcines a mixture of 408 gypsum with 148 ferric oxide at 800° to 1500°, and passes the mixture of SO_2 and O thus obtained over oxides of manganese, tungsten, molybdenum or thorium at a temperature above 200°, in order to start the combination of SO_2 and O.

Wedekind & Co. (Ger. P. 232784) roast a mixture of calcium sulphate, sand, and so much pyrites that the heat produced by the burning of the latter is sufficient to effect the decomposition of the $CaSO_4$ by SiO_2. The B. P. is 20186 of 1910 and the Fr. P. 419871. The U.S. P. of F. Meyer and Wedekind & Co., 1008847, is for the same process.

[1] *Wagner's Jahresber.*, 1858, p. 95.
[2] *Ibid.*, 1865, p. 271.
[3] *Dingl. polyt. J.*, 221, 442.
[4] *Bull. Soc. Chim.*, 21, 47.

Hilbert (Ger. P. 207761) makes SO_3, together with glass, by heating calcium sulphate with sand and alkaline sulphates.

Trey [1] describes his laboratory experiments on the production of sulphuric acid from gypsum by heating with pure silica or sand, also with addition of 0·5 per cent. ferric oxide. In all cases the reaction took place fairly quickly and practically completely, but the H_2SO_4 driven out was decomposed at the high temperature of the process into SO_2, O, and H_2O, so that the gases would have to be subjected to a catalytic process, in order to obtain SO_3 or H_2SO_4.

B. Dirks (Ger. P. 295906 of 1915) decomposes ammonium sulphate, prepared by the action of ammonia and carbon dioxide gases on gypsum or anhydrite, with phosphoric acid, the resultant sulphuric acid being free from arsenic and selenium. The residual ammonium phosphate is decomposed by heat and the ammonia and phosphoric acid recovered.

His later patent (301791 of 1917) describes a process of treating gypsum or anhydrite (which are transformed by known methods into ammonium sulphate) by mixing them with metallic oxides, especially iron oxide or hydroxide (*e.g.* limonite), the mixture being slowly heated to 250° until the ammonia is expelled. On further heating to redness, sulphur trioxide is evolved in almost quantitative yield. The residue of iron oxide is moistened with water and used again in the process.

In the *Report of the Chemical Mission*, p. 48, to the Farbenfabriken vorm. Friedr. Bayer & Co., Leverküsen, the process for production of sulphuric acid from gypsum is described. The plant is essentially that of a cement works employing rotary kilns. The kiln used is about 164 ft. long by 10 ft. diameter, and is cooled by water-drips at the length next to the burner, in which coal-dust firing is used. The charge admitted to the kiln is calcium sulphate from the filter press and silica, with a proportion of clay and powdered coal. Efforts were made to obtain further details about the composition of the furnace charge, but these were withheld. The gases obtained were stated to contain from 6 to 7 per cent. SO_2. They were carried in a long upward sloping tunnel, apparently of steel, about 3 ft. diameter and 400 to

[1] *Z. angew. Chem.*, 1909, pp. 2375-2377.

500 ft. long. After being scrubbed and dried, the gas is passed to the contact plant. The residue from the furnace is cooled and discharged in the same manner as cement clinker, and was shipped to unoccupied territory for cement manufacture. The general exit from the contact plants is obviously high in acid content—a fact stated to be brought about by working the calcium sulphate process. It was stated that the process is considered to be economically possible when the cost of transporting pyrites is high and calcium sulphate is available.

In an article in the *J. Soc. Chem. Ind.*, 1920, p. 47R, E. V. Evans mentions, when dealing with the chemical industry of Germany, that a director had personally dealt with the manufacture of sulphuric acid from gypsum, and he had apparently done nothing else for years. When it was suggested that this process had been evolved only for the purpose of relieving Germany from the temporary difficulty of obtaining pyrites or other sources of sulphur, he emphatically stated that there should be a much larger future for this process than the present cost-sheets showed, owing to the fact that the reduction mass resulting from the roasting of gypsum with low quality fuel was most eagerly sought for by the manufacturers. It was this which, in his opinion, determined the future of the process.

W. Dominik[1] states that gypsum may be converted into ammonium sulphate, and the latter into $NaHSO_4$, from which free sulphuric acid may be obtained by (1) reduction of the free acid to sulphur dioxide and re-oxidation; (2) distillation with ballast (*cf.* Moscicki and Dominik, *Chem. Abs.*, **15**, 2166); (3) crystallisation of hydrated sulphate of soda by cooling and concentration of the mother liquor. Sulphate of soda increases in solubility with addition of free sulphuric acid to a maximum above which acid sulphate separates. The solubility also decreases rapidly with the temperature; at -11° the maximum solubility corresponding to 32 per cent. free acid is only about 4 per cent. sodium sulphate by weight, so that at this temperature a fairly complete separation can be obtained in one operation. A calculation of the water required and fuel consumption necessary for decomposition of the acid salt at a given temperature is added.

[1] *Przenysl. them.*, 1921, 5, 185-91; *Chem. Abs.*, 17, 1692 (1923).

Employment of Bisulphates (Nitre-cake, etc.).—The Soc. Dior fils (Fr. P. 417816) makes sulphuric acid from alkaline sulphates or bisulphates, to which is added bauxite or aluminium sulphate, by heating in a muffle, so as to liberate SO_2 and SO_3, which are then transformed into pure concentrated sulphuric acid. The aluminium sulphate, etc., is extracted from the residue with water, and is treated with CO_2 to obtain an alkaline carbonate. An addition to this patent provides for the addition of coke-dust to the mixture described above; this mixture is heated to 1100° to 1250° in a muffle-furnace. When the mixture begins to lose its black colour and white specks appear, it is withdrawn from the furnace and treated as above.

Zahn (Fr. P. 389898; U.S. P. 921329) adds to sodium bisulphate just sufficient water to form hydrated sulphuric acid and the normal sulphate, say 6 or 7 kil. water to 100 bisulphate. Part of the sulphuric acid escapes on heating, whilst the mixture becomes pasty, and in this state is introduced into a muffle and calcined.

Prud'homme (Fr. P. 400030) obtains SO_3, or a mixture of SO_2 and O, by heating natural or artificial sulphates in an electric furnace with simultaneous formation of anhydrous bases. By adding SiO_2, or Al_2O_3, or Fe_2O_3 to the sulphates, the decomposition of the latter is rendered more complete.

Uebel (Ger. P. 226110) exposes bisulphate in a finely divided state to the action of superheated air, or steam, or fire gases, in a tower, the bottom of which consists of a calcining-hearth.

Benker (B. P. 1844 of 1907; Ger. Ps. 204354 and 204703; U.S. P. 899284; Fr. P. 381863) mixes nitre-cake with fine sand, or finely divided silicates, or anhydrous sulphates of Na, K, or Ca, in such proportions that the mass does not fuse on heating. Sulphuric acid may be distilled off and anhydrous Na_2SO_4 remains behind, without the destruction of the apparatus, which takes place when the bisulphate by itself is strongly heated.

Rogé (B. P. 124988) describes a process in which about 5 per cent. of pulverised charcoal or sawdust is incorporated with acid sodium sulphate, and the mixture is formed into lumps or slabs, which are burned in a kiln with free access of air, the acid gases being collected in the usual manner.

Dawson (B. P. 127677) dissolves nitre-cake or other acid sodium sulphate in water to obtain a liquor having a concentration predetermined according to the composition of the acid sodium sulphate and the temperature to which the liquor is to be cooled. The liquor is then cooled to a temperature below 0°, which effects a separation of Glauber salts, leaving a mother liquor having a maximum ratio of sulphuric acid to sodium sulphate. If a more concentrated solution is under treatment, cooled water is added during the cooling, in quantity dependent on the original composition of the solution and the degree of cooling.

According to the *Chem. Trade J.*, 1918, p. 176, a process for the manufacture of sulphuric acid from nitre-cake is the subject of B. P. 117649, assigned to F. A. Freeth of Winnington, Cheshire. The process depends upon the fact that when a solution of nitre-cake in water is allowed to react with calcium sulphate, a double salt of the composition $CaSO_4$, Na_2SO_4 (calcium sodium sulphate or "glauberite") is formed, free sulphuric acid being liberated. The reaction proceeds to an extent which renders practicable the subsequent separation of pure, or nearly pure, sulphuric acid. The process is carried out as follows:—

Sufficient quantities of water, nitre-cake, and calcium sulphate are allowed to react to yield, at the particular temperature chosen for the reaction (50°, for example, being a suitable temperature), a solution saturated, or practically saturated, with acid sodium sulphate ($NaHSO_4$), the double salt $CaSO_4$, Na_2SO_4, and calcium sulphate; a small amount of calcium sulphate is also present in the solid form.

The precipitate, consisting essentially of a large quantity of calcium sodium sulphate admixed with a small quantity of calcium sulphate, is removed by any well-known means, and the remaining solution cooled to ordinary temperatures, when a precipitation of acid sodium sulphate takes place, which is separated from the solution. The liquid remaining is then concentrated until it contains preferably between 70 and 75 per cent. of sulphuric acid, and cooled to a temperature which should not exceed 50°, but preferably to atmospheric temperature, when it deposits practically all the remaining sodium sulphate in the form of a salt having the composition Na_2SO_4.

$3H_2SO_4$, $2H_2O$, which is separated, leaving a solution of about 75 to 80 per cent. of sulphuric acid containing less than 1 per cent. of sodium sulphate, which can be used either as it is or further concentrated.

The sulphuric acid contained in the $NaHSO_4$, and in the salt Na_2SO_4, $3H_2SO_4$, $2H_2O$, which are respectively precipitated in the course of the process, is recovered in a subsequent cycle of operations, by allowing these salts, together with nitre-cake, to react with calcium sulphate for the preparation of calcium sodium sulphate, and so on, as already described.

Calcium sulphate and sodium sulphate may be recovered from the calcium sodium sulphate by extracting the latter with hot water, whereby it is decomposed, sodium sulphate going into solution and the greater portion of the calcium sulphate remaining undissolved.

As an example of the process in operation, 689 parts by weight of $NaHSO_4$, 180 parts of H_2O, and 313 parts of $CaSO_4$ are stirred together at a temperature of 50°. When the reaction is finished, the resulting solution is saturated with respect to $CaSO_4$, the double salt $CaSO_4$, Na_2SO_4, and $NaHSO_4$, and has the following composition :—$CaSO_4$, trace ; Na_2SO_4, 15·5 per cent. by weight ; H_2SO_4, 51·5 per cent. ; H_2O, 3·0 per cent. A precipitate of calcium sodium sulphate mixed with a little calcium sulphate is also formed. The precipitate is removed, and the solution which, after removal of the precipitate, contains 52 per cent. by weight of H_2SO_4, is cooled to 25°, when acid sodium sulphate is deposited, and the solution contains 56 to 57 per cent. H_2SO_4. The precipitate is removed and the solution then concentrated until it contains 75 per cent. by weight of sulphuric acid. It is then again cooled to 25°, when it deposits the salt Na_2SO_4, $3H_2SO_4$, $2H_2O$: the solution then contains 79 to 80 per cent. of sulphuric acid, and about 0·5 per cent. Na_2SO_4.

In solutions saturated with respect to $CaSO_4$, the double salt $CaSO_4$, Na_2SO_4, and $NaHSO_4$ at temperatures which are considerably higher or lower than 50°, the ratio of sodium sulphate to sulphuric acid is less favourable to the economy of the process.

L. T. Sherwood (U.S. P. 1255474 of 1918) utilises the heat of combustion of sulphur to convert nitre-cake into normal

sodium sulphate and SO_3. The former product is recovered as normal sodium sulphate, and the latter, with the sulphur gases, as sulphuric acid.

E. R. Watson[1] suggests that sulphuric acid can be produced in India from the sulphate of soda found in the earth salts of Behar. By the electrolysis of 40 per cent. aqueous sodium sulphate solution, employing a platinum, iron, or copper cathode and a platinum, lead, or carbon anode, a current density of about 4 amperes per sq. decimetre and a potential difference between the electrodes of about 5 volts, starting the electrolysis at about 30° and allowing the temperature to rise to about 40°, conversion into sodium hydroxide and sulphuric acid can be effected with a current efficiency of about 90 per cent. and an energy efficiency of about 50 per cent., provided electrolysis is not carried beyond an average conversion of about 25 per cent. Nearly all the sodium sulphate may be crystallised out of the alkaline liquor, leaving sodium hydroxide in the mother liquor nearly pure, and sodium hydrogen sulphate may be similarly obtained from the acid liquor. Sulphuric acid is best produced from the sodium hydrogen sulphate by distillation.

Another very interesting paper is given by Harold V. Atwell and Tyler Fuwa (*Ind. and Eng. Chem.*, 1923, **15**, 617-620).

III. Calcining Pyrites with Salt.

Kenyon and Swindells (B. P. of 21st May 1872) calcine the chlorides of sodium or potassium with iron- or copper-pyrites, and treat the gas with nitric or chromic (!) acid in high towers in order to convert the sulphurous into sulphuric acid; at the same time chlorine is given off. Wagner[2] points out that in this process the sulphuric acid must remain behind in the form of alkaline sulphates.

[1] *Chem. Age*, 1923, **8**, 608; *J. Soc. Chem. Ind.*, 1923, **42**, 251-2T; *J. Chem. Soc.*, 1923, pp. ii, 457.

[2] *Jahresber.*, 1874, p. 272.

IV. By Producing Hydrochloric and Sulphuric Acids Simultaneously.

Hähner (B. P. of 28th March 1854) employs chlorine in the presence of aqueous vapour for oxidising SO_2. The same process has been patented by Macfarlane (B. P. of 14th January 1863).

The Consortium für elektrochemische Industrie at Nürnberg (Ger. P. 157043) produces at the same time sulphuric and hydrochloric acid by allowing a mixture of SO_2 and chlorine to act upon water or aqueous hydrochloric acid in such quantities that, on the one hand, highly concentrated sulphuric acid, free from HCl, flows out, and, on the other hand, gaseous HCl escapes from the apparatus, according to the well-known reaction: $SO_2 + 2H_2O + Cl_2 = SO_4H_2 + 2HCl$. The hitherto difficult separation of hydrochloric and sulphuric acid is effected by employing a "reaction-tower," filled with stones, into which pyrites-burner gases and chlorine enter, and which is fed with only so much water as corresponds to the formation of gaseous HCl and sulphuric acid of 65 to 80 per cent. According to the Ger. P. 157044 of the same firm, an excess of chlorine is employed, which produces hydrochloric acid free from sulphuric acid, whilst, when working according to the first-mentioned patent, in the case of irregular currents of gas, SO_2 and Cl may get into the condensers for HCl and there form H_2SO_4, which contaminates the hydrochloric acid. This is avoided by working with an excess of chlorine. Their B. P. 14342 of 1902, taken out together with Askenasy and Mugdan, is for the same process.

Further details of this process are given by Bernard Neumann and Franz Wilczewski, *Z. angew. Chem.*, **36**, 377-381 (1923).

Tobler (U.S. P. 1332581) employs exactly the same reaction. His apparatus consists of three absorbing towers constructed as Glovers, a number of tourills, and a fourth Glover tower. SO_2 is delivered to the first tower, where a part of the heat is utilised in concentrating and in removing the hydrochloric acid from the sulphuric acid formed later in the process. Upon the gas passing to the second tower, it is mixed with chlorine from the electrolytic cells. The reaction

is completed in the third tower, and the gases are drawn through the tourills and fourth tower by means of the fan.

V. From Sulphur Dioxide and Selenium Dioxide.

P. C. Haesler (U.S. P. 1341462, assignor to the Liberty Laboratories, Inc., May 25, 1920) describes a new method of preparing sulphuric acid. Instead of oxidising SO_2 with the oxides of nitrogen, selenium dioxide is used according to the equation :—

$$2SO_2 + H_2O + H_2SeO_3 = 2H_2SO_4 + Se.$$

The selenium is filtered and reoxidised. A 50 per cent. sulphuric acid free from selenium can thus be obtained without pressure. Anode slimes and other impure selenium sources can be used for the source of selenium, as roasting these will yield an oxide sufficiently pure for the above reaction.

VI. Combination of the Contact-process and the Chamber-process.

Wilde[1] passes the pyrites-burner gases into a shaft, filled with ferric oxide contact-mass, where about 30 per cent. of the SO_2 is converted into SO_3, and then by means of a fan through a Glover tower and into lead-chambers. By this combination the work done by the chambers is increased by at least 30 per cent., more uniform results are obtained, and 30 per cent. of the nitre is saved. All the acid can be brought in the Glover to 60° Bé. and upwards, and can be obtained colourless. The ferric oxide removes also some of the arsenic present, and at the same time acts as a dust-catcher.

The drawback of towers of this description results from insufficient draught due to the resistance of the contact-mass, making the use of high-speed fans necessary.

In order to obtain the most effective conversion of the SO_2, a considerable depth of this mass is desirable, dryness of pyrites and air being also essential.

[1] *Eighth Int. Cong. Appl. Chem.*, 1912, **2**, 249; Abstr. in *J. Soc. Chem. Ind.*, 1912, p. 876.

CHAPTER VII

APPLICATIONS OF SULPHURIC ACID

ACCORDING to H. J. Bailey,[1] the amounts of sulphuric acid used per annum in Great Britain amongst the various industries for the years 1916 to 1918 are as follows:—

	1916.	1917.	1918.
Explosives	352,131	337,765	152,193
Dyes	17,736	9,688	9,143
Accumulators	2,696	3,145	3,075
Alum	24,854	24,406	26,184
Bichromates	8,433	5,710	5,316
Bleaching powder	70,413	50,302	50,694
Copper and copper pickling	3,360	2,702	1,339
Copper sulphate	21,705	27,032	30,424
Drugs and fine chemicals	3,098	4,479	4,225
General chemicals	9,203	9,217	9,624
Chemical warfare	39	1,122	1,678
Hydrochloric acid	71,872	53,510	52,227
Iron pickling	54,523	28,864	28,840
Metal trades	3,615	3,263	2,396
Mineral waters	2,421	490	391
Oil-refining	23,690	17,022	14,840
Paints and antimony colours	4,081	3,667	3,684
Sewage	442	307	723
Soap and glycerine	2,608	4,060	3,560
Sugar-refining	925	1,051	1,067
Sulphate of ammonia	235,340	230,145	231,092

(Later returns (1922) show a considerable decrease in the consumption of acid used in the manufacture of explosives, namely, one-tenth of the amount shown for 1918, but the consumption in the production of dyes is more than double: for sulphate of ammonia a 30 per cent. increase; the textile trades four times; oil-refining two and half times; hydrochloric acid 50 per cent. more; and for mineral waters the amount reaches the figure for 1916.—W. W.)

[1] *J. Soc. Chem. Ind.*, 1921, p. 246R.

	1916.	1917.	1918.
Sulphates of magnesium and zinc .	8,347	9,235	8,339
Sulphites and phosphates . .	10,717	11,000	12,504
Sundries	6,639	5,560	6,006
Superphosphates and compound manures.	169,730	212,209	270,597
Tar	13,704	14,946	13,897
Textile industries	23,211	15,987	13,323
Totals . .	1,163,533	1,086,894	957,381

The production of sulphuric acid in terms of 100 per cent. acid, all of which was produced by the chamber-process, for the years 1915 to 1918, is as follows :—

1915.	1916.	1917.	1918.
1,050,000 tons	1,208,275 tons	1,160,789 tons	964,158 tons

United States.

According to L. B. Skinner,[1] prior to the war, sulphuric acid in the United States was made exclusively from the gases produced by roasting zinc-blende and pyrites of the blast-furnace treatment of Tennessee copper ores. The demand for acid during the war greatly stimulated production, which, however, never met all requirements. In order to increase the output from zinc-acid plants, brimstone was added to the ore fed into the burners (Hegeler kilns), whereby the chamber output was increased 20 per cent. Australian concentrates were used and may continue to be used. The production from plants then using, or which previously used pyrites, was also increased to some extent by the substitution of brimstone for the now scarcer Spanish ore.

Very little extension in the use of pyrrotite ores has taken place, but it is considered that, if ground finely and mixed with some crude sulphur, this mixture will produce a gas suitable for many of the existing acid plants.

According to the *U.S. Geol. Surv.*, 1917, p. 61, the raw materials used in the manufacture of acid in 1917 were as follows :—

Sulphur . . .	483,837 long tons.
Pyrites . . .	257,138 „ „

[1] *Chem. and Met. Eng.*, 1918, **18**, 82-5.

Gold- and silver-bearing pyrites and galena, 17,380 tons; copper-bearing sulphides, 856,033 tons; and zinc-bearing sulphides, 736,911 tons.

QUANTITIES OF SULPHURIC ACID PRODUCED IN THE U.S. FROM DIFFERENT RAW MATERIALS FOR 1914, 1917, AND 1918.[1]

	1914.	1917.	1918.			
From brimstone . .	100,000	2,350,000	3,580,000	2·6	32·6	48·0
From pyrites—						
Spanish . . .	1,900,000	1,650,000	570,000	50·0	22·9	7·6
Domestic, including coal, brasses, and pyrrhotite . .	600,000	850,000	950,000	15·8	11·8	12·7
Canadian py. . .	300,000	500,000	550,000	7·9	6·9	7·5
Zinc ores . . .	500,000	1,300,000	1,200,000	13·2	18·1	16·1
Waste gases from copper-smelters . . .	400,000	550,000	600,000	10·5	7·7	8·1
Totals . .	3,800,000	7,200,000	7,450,000	100·0	100·0	100·0

According to the *U.S. Bureau of Mines*, No. 184, the production of sulphuric acid in U.S.A. in 1865 was only 37,500 tons (as 100 per cent. acid); in 1880, 265,630; and in 1900, over one million tons.

1913 . .	2,239,930	1916 . .	3,938,000
1914 . .	2,280,000	1917 . .	4,505,000
1915 . .	3,173,800	1918 . .	4,661,300

At the conclusion of the armistice the production in U.S.A. was at the rate of about six million tons (1918), 40 per cent. of which was produced by the contact-process.

The proportion in which the various industries were using acid in 1918 is shown below:—

Explosives	33·5 per cent.
Domestic	2·5 ,,
Fertilisers (superphosphates) . . .	28·4 ,,
Oil refineries	8·8 ,,
Chemicals, drugs, am. sulphate . .	9·9 ,,
Steel pickling and galvanising . . .	9·3 ,,
Fabrics, textiles	1·4 ,,

[1] According to *Chem. and Met. Eng.*, 25, 861: Andrew M. Fairlie.

Paints, lithopone, glue, etc.	1·3 per cent.
Metallurgical, inc. storage batteries	3·9 ,,
Miscellaneous	1·0 ,,
	100·0

World's Production of Sulphuric Acid.

According to the *Chem. and Met. Eng.*, **21**, 400, the world's pre-war acid production (1913) was as follows:—

U.S.A.	2,200,000
Germany	1,600,000
Great Britain and Ireland	1,150,000
France	875,000
Other countries	4,675,000
	10,500,000

APPENDIX

FIRST AID IN ACID BURNS.

ACCORDING to the *Chem. Trade J.*, 1920, p. 584, the treatment of acid burns was described by A. K. Smith, manager of the medical section of E. I. du Pont de Nemours & Co., in a paper read before the recent annual Congress of the National Safety Council held at Milwaukee, in the United States. He stated that the wounds caused in tissues by acids and alkalies are not strictly burns, according to the accepted definition of the term. Strong sulphuric acid, nitric acid, etc., when applied to living tissue, cause its destruction and produce a sloughing.

Smith gave the following suggestions for first aid :—To be of any value it must be immediate aid, and probably the most valuable is the shower bath, which must be used before any attempt is made to remove clothing. A solution of bicarbonate of sodium may be mopped on the burned area. After this has been liberally carried out, the patient should be placed in a physician's care. In simple burns, the burned area may be mopped with dry gauze and an ointment applied, such as boric-acid ointment or burn ointment, which is made of bicarbonate of soda and petroleum, or oxide of zinc ointment. A liberal layer of the ointment should be spread on gauze and held in place with a gauze bandage. This dressing relieves the pain, and is sufficient if the dressing is renewed occasionally.

In more severe burns, the wound should be cleansed of all loose rolled-up skin, mopped with a mild antiseptic such as boric-acid solution, and an ointment applied on gauze and held in place by a rather loose gauze bandage. Blisters are generally caused in cases of severe burns. Small unruptured ones should be left alone ; the larger ones, where their tension is likely to cause pain, are opened. The area should first of all be sterilised with a $3\frac{1}{2}$ per cent. alcoholic solution of iodine and a liberal incision then made with a sterilised knife near the edge of the blister, allowing its top to collapse and remain.

The ointment used in dressing these cases should be absolutely clean, sterile, and mildly antiseptic, and should spread with ease. The dressings are renewed more often when discharges are profuse, and later at as long intervals as possible, in order to allow healing to progress without disturbance.

Very severe burns are cleansed of all loose detritus and dressed with a sterile ointment, as in second-degree burns. After three or four days the ointment dressing is replaced by a wet gauze dressing, using a sterile, normal, salt solution. The dressing must be kept wet by repeated applications of the salt solution. A slough forms in these cases, necessitating a long wait until the sound tissue loosens and throws out the dead material, and all this must occur before healing takes place to any extent. The use of wet dressings leaves the wound in a very favourable condition for skin grafting, should this become necessary. The long time required for healing in these cases is due to the slow separation of the slough, and after that has taken place, granulation tissue must fill up the sloughed-out spaces and a new epidermis grow to cover the entire area. Healing may be hastened by a careful removal of portions of the slough when re-dressings are being made, also by keeping down excessive or exuberant granulation tissue growth, and most important of all by skin-grafting. The making of numerous small pin-point grafts, some of which will grow, will reduce the time of ultimate closure of the wound. Shock may be the accompaniment of the severer burns, and should be *combated* by a hypodermic injection of morphine.

The patient is wrapped in hot blankets and surrounded with hot bottles or hot bricks. Care should be taken to cover the warming bricks or bottles with flannel or other material to prevent burning the patient. *Salt* solution may be introduced into the system by one of the various methods in order to increase the volume of blood. Ordinary stimulants given by the stomach are of little value in this condition.

Burns of the eyes should be treated by douching the eyes with a solution of bicarbonate of soda, after which a piece of boric-acid ointment, about the size of a pea, is put under the eyelid and carefully worked into all corners by gentle manipulation on the outside. Further treatment of the eyes can best be done by an eye specialist.

Sulphuric Acid Gravities at Various Temperatures.

°Tw. read off.	At Temperatures: 20	25	30	35	40	45	50	55	60	65	70	75	80
	° Twaddells @ 15° C.												
168	...	...	...	...	...	...	...	...	...	...	...	...	...
167	168	...	...	...	...	...	...	...	...	...	...	...	...
166	167	168	...	...	...	...	...	...	...	...	...	...	...
165	166·1	167·1	168·2	...	...	...	...	...	...	...	...	...	...
164	165·1	166·1	167·2	168·2	...	...	...	...	...	...	...	...	...
163	164	165·1	166 2	167·2	168·2	...	...	...	...	...	...	...	...
162	163·1	164·1	165·2	166·3	167·3	168·3	...	...	...	...	...	...	...
161	162·1	163·1	164·2	165·3	166·4	167·3	168·3	..	...	...	...	...	...
160	161·1	162·2	163·2	164·3	165·4	166·4	167·4	168·5	...	...	...	...	...
159	160·1	161·2	162·2	163·3	164·4	165·4	166·4	167·5	168·5	...	...	...	...
158	159·1	160·2	161·2	162·3	163·4	164·5	165·5	166·6	167·6	168 7	...	...	...
157	158·1	159·2	160·2	161·3	162·4	163·5	164·5	165·7	166·7	167·8	168·8	...	...
156	157·1	158·2	159·2	160·3	161·4	162·5	163·5	164·6	165·7	166·8	167·8	168·9	...
155	156·1	157·2	158·2	159·3	160·3	161·4	162·5	163·6	164·7	165·8	166·8	167·9	168·9
154	155·1	156·2	157·2	158·3	159·3	160·4	161·5	162·6	163 6	164·7	165·7	166·8	167·8
153	154·1	155·1	156·2	157·2	158·3	159 4	160·4	161·6	162·6	163·7	164·7	165·8	166·7
152	153·1	154·1	155·2	156·2	157·3	158·4	159·4	160·5	161·5	162·6	163·6	164·7	165·7
151	152·1	153·1	154·2	155·2	156·3	157·4	158·4	159·5	160·5	161·6	162·6	163·7	164·7
150	151·1	152·1	153·2	154·2	155·3	156·4	157·4	158·5	159·5	160·6	161·6	162·6	163·6
149	150·1	151·1	152·2	153·2	154·2	155·3	156·3	157·3	158·4	159·4	160·4	161·5	162·5
148	149·1	150·1	151·2	152·2	153·2	154·3	155 3	156·3	157·3	158·3	159·3	160·4	161 4
147	148	149·1	150·1	151·1	152·1	153·2	154·2	155·2	156·2	157·2	158·3	159·3	160·3
146	147·0	148·0	149·1	150·1	151·1	152·2	153·2	154·2	155·2	156·2	157·2	158·2	159·2
145	146	147	148	149	150	151	152	153	154	155	156	157·1	158
144	145·0	146	147	148	149	150	151	152	153	154	155	156	157
143	144	145	146	147	148	149	150	150·9	151·9	152·9	153·9	154·9	155·9
142	143	144	145	146	146·9	147·9	148·9	149·8	150·8	151·8	152·8	153·8	154·8
141	142	143	144	145	145·9	146·9	147·9	148·8	149·8	150·7	151·7	152·8	153·8

140	141	142	143	143·9	144·9	145·9	146·8	147·8	148·7	149·7	150·7	151·7	152·6
139	140	141	142	142·9	143·9	144·8	145·8	146·7	147·7	148·7	149·7	150·6	151·6
138	138·9	139·9	140·9	141·8	142 8	143·8	144·8	145·7	146·6	147·6	148·6	149·6	150·5
137	137·9	138·9	139·9	140·8	141·8	142·8	143·8	144·7	145·6	146·6	147·6	148·5	149·4
136	136·9	137·9	138·9	139·8	140·8	141·8	142·7	143·7	144·6	145·6	146·5	147·5	148·4
135	135·9	136·9	137·9	138·8	139·8	140·7	141·7	142·6	143·6	144·5	145·5	146·4	147·3
134	134·9	135·9	136·9	137·8	138·8	139·7	140·7	141·6	142·6	143·5	144·4	145·3	146 3
133	133·9	134·9	135·9	136·8	137·8	138·7	139·7	140·6	141·5	142·4	143·3	144·3	145·2
132	132·9	133·9	134·9	135·8	136·8	137·7	138·7	139·6	140·5	141·4	142·3	143·2	144·1
131	131·9	132·9	133·9	134·8	135·7	136·7	137·6	138·6	139·5	140·4	141·3	142·2	143·1
130	130·9	131·9	132·8	133·8	134·7	135·7	136·6	137·5	138·4	139·3	140·2	141·1	142·0
129	129·9	130·9	131·8	132·8	133·7	134·7	135·6	136·5	137·4	138·3	139·2	140·1	141·0
128	128·9	129·9	130·8	131·8	132·7	133·7	134 6	135·5	136·4	137·2	138·1	139·1	140·0
127	127·9	128·9	129·8	130·8	131·6	132·6	133·5	134·4	135·3	136·2	137·1	138·0	139·0
126	126·9	127·9	128·8	129·7	130·6	131·5	132·4	133·3	134·2	135·1	136·1	137·0	137·9
125	125·9	126·9	127·8	128·7	129·6	130·5	131·4	132·3	133·2	134·1	135·1	136·0	136·9
124	124·9	125·8	126·8	127·7	128·6	129·5	130·4	131·2	132·1	133·1	134·0	135·0	135·8
123	123·9	124·8	125·7	126·6	127·5	128·4	129·4	130·2	131·1	132·0	132·9	133·8	134·7
122	122·9	123·8	124·7	125·6	126·5	127·4	128·3	129·2	130·1	131·0	131·9	132·8	133·7
121	121·9	122·8	123·7	124·6	125·5	126·4	127·3	128 2	129·1	130·0	130·9	131·8	132·7
120	120·9	121·8	122·7	123·6	124·5	125·4	126·3	127·2	128·1	129·0	129·9	130·8	131·7
119	119·9	120·8	121·7	122·6	123·5	124·4	125·3	126·2	127·0	128·0	128·8	129·8	130·7
118	118·9	119·8	120·7	121·6	122·5	123·4	124·3	125·2	126·0	126·9	127·8	128·7	129·6
117	117·9	118·8	119·7	120·6	121·5	122·4	123·3	124·2	125·0	125·9	126·8	127·7	128·6
116	116·9	117·8	118·7	119·6	120·5	121·3	122·3	123·2	124·0	124·9	125·8	126·7	127·6
115	115·9	116·8	117·7	118·6	119·5	120·3	121·2	122·1	123·0	123·9	124·7	125·7	126·6
114	114·9	115·8	116·7	117·5	118·4	119·3	120·2	121·1	121·9	122·8	123·7	124·7	125·6
113	113·9	114·8	115·7	116·5	117·4	118·3	119·2	120·1	120·9	121·8	122·8	123·7	124·6
112	112·9	113·8	114·7	115·5	116·4	117·2	118·1	119·1	119·9	120·8	121·7	122·7	123·6
111	111·9	112·7	113·6	114·5	115·3	116·2	117·1	118·0	118·8	119·7	120·7	121·6	122·5
110	110·9	111·7	112·6	113·4	114·3	115·2	116·0	116·9	117·7	118·6	119·5	120·3	121·2

The above Table, calculated from J. Domke's data, shows at a glance the °Tw. of the acid at 15° C. when the reading is taken at temperatures from 20° to 80°.

Col. 1 is the °Tw. read off, and opposite, under the temperature at which the reading is taken, the °Tw. at 15° C. is shown. Domke's figures differ somewhat from those given, Vol. I, p. 207, which were averages only.

Cements and Packings.

Mixtures used.	Character and Uses.	
Flint dust and silicate of soda.	Joints for earthenware.	Unaffected by acids, but difficult to remove from the joints.
Pumice powder and silicate of soda.	For brick joints, tiles, earthenware pipes, Volvic stone.	Useful for sulphuric acid.
Asbestos powder 1 part, barytes 1 part, silica water 2 parts, silicate of soda 1 part, and water 6 parts.	For mending cracks in silica or earthenware apparatus.	Permanent in the joints of pipes, etc.
Red lead and glycerin.	Ironac or other acid-resisting ironwork.	Sets hard after a time.
Silicate of soda, short asbestos fibre, and 5 per cent. of mineral oil.	For pipes conveying nitric-acid vapours.	
Asbestos powder 3 parts, barytes 1 part, and made into thick putty with silicate of soda.	For joints of glass-ware.	
China clay, French chalk or asbestos, and silicate of soda.	For general luting purposes for acids.	
China clay and tar.	For iron burner pipes.	
Fireclay and silicate of soda.	For general luting purposes.	
Plaited blue asbestos soaked in hot paraffin.	For bearings of centrifugal pumps.	

Weight per yard of Lead Piping for Chemical Purposes.

Bore in Inches.	Light.		Medium.		Heavy.	
	Thickness, in.	Weight, lbs.	Thickness, in.	Weight, lbs.	Thickness, in.	Weight, lbs.
½	·13	3·81	·18	5·69	·23	7·81
¾	·14	5·43	·19	8·31	·25	11·64
1	·14	7·43	·20	11·17	·27	15·96
1¼	·15	9·77	·22	15·05	·29	20·79
1½	·16	12·36	·23	18·52	·31	26·12
2	·17	17·17	·25	23·05	·33	35·79
2½	·18	22·45	·26	33·40	·35	46·43
3	·20	29·79	·28	42·75	·37	58·04

Formula: 15·517(D − t)t, where D = external diam. in inches, and t = thickness in decimals of an inch.

Weight of Sheet Lead.

Standard weight in pounds per square foot. Thickness in decimals of an inch.

Wt.	Th.	Wt.	Th.	Wt.	Th.	Wt.	Th.	Wt.	Th.	Wt.	Th.
2·5	·042	4	·068	6	·102	8	·136	10	·170	14	·238
3	·051	5	·085	7	·119	9	·153	12	·203	16	·271

INDEX OF NAMES

ABRAHAM, 55, 135, 292
Accrington Brick and Tile Co., Ltd., 237, 239
Aktien-Gesellschaft für Bergbau, Blei- und Zinkfabrikation, 223
Anzies, 394
Appleton & Howard, 164
Archereau, 394
Arsonval, 345
Askenasy, 367, 401
Atwell, H. V., and Tyler Fuwa, 400
Awe, 32

BADISCHE ANILIN- UND SODA-FABRIK, 184, 205
Bailey, H. J., 45, 289, 403
Barbiers, 79
Barruel, 362
Basset, 391
Baudisch and Klinger, 307
Bayer & Co., 162, 395
Beck, J. A., 209
Bender, 388
Benker, 16, 27, 39, 47, 131, 199, 202, 220, 229, 277, 279, 397
Benker and Hartmann, 89, 118, 135, 194, 295
Benker & Millberg, 47, 112, 186
Berl and Innes, 236
Berzelius, 309, 316, 370
Bettenhausen, 243
Bithell and Beck, 236, 352
Blau, F., 56
Blondlot, 342
Bloxam, 340
Bode, Fr., 197, 206, 224, 362
Böhringer and Söhne, 390
Borsig, A., 190
Bourdon, 139
Bradley, 392
Bressanin, 372
Brialle, 372, 391
Briegleb, 161
Briggs, 168
Briner and Fridöri, 333
Briner and Rossignol, 334
Brivet, 199
Brode, 326
Bruckhardt, 86
Brulfer, 53
Büchner, 343
Buckley Brick and Tile Co., Ltd., 212, 246
Budenberg Gauge Co., Ltd. (Broadheath, Cheshire), 105
Buff, H., 389
Burgemeister, 55
Bussy and Buignet, 342

CARMICHAEL & CO., LTD., 33, 241
Carmichael and Guillaume, 87
Carpenter, R. F., 303, 306
Chance & Hunt, Ltd., 56, 82
Chemical Pump and Valve Co., 165
Chemische Fabrik Griesheim-Elektron, 80, 345
Clark, 388
Clark, G. E., 352
Clément and Désormes, 309
Coehn and Becker, 389
Consortium für Elektrochemische Industrie, 401
Cortin Ltd., J., 164
Cox, 287
Cresse, 8
Crowder, 195, 203, 263, 293
Crowther, 344
Cummings, 394
Curtius & Co., Fr., 89

DAVIDSON, C., 103
Davis Bros., 360
Davis, G. E., 56, 198, 287, 297, 355, 363
Davis, G. E. and A. R., 43
Davison & Co., Ltd., 212, 248
Davy, H., 309, 315
Dawson, 54, 398

Deacon, 388
Deimler, 185
Delplace, 120
Delplace, E. and T., 58
Delplace, M., 127, 283
Denberg, Van, 394
Deutecom, 335
Deutsch, 366
Deutsche Ton- und Steinzeugwerke, 184
Deville, 389
Dior, R., 56
Dior fils, 397
Dirks, B., 395
Dittmar, 371
Divers, 307, 328
Dominik, W., 396
Donnan, F. G., and I. Masson, 251
Doulton & Co., Ltd., 171
Dupasquier, 346
Durand, Huguenin & Co., 79
Duriron Co., 187
Düron, 87, 119

ERSTE OESTERREICHISCHE SODA-FABRIK, 81
Eschellmann, 285, 287
Evans, E. V., 396

FAIRLIE, A. M., 164, 241, 405
Falding, F. J., 20, 58, 127, 132, 135, 154, 242, 339, 379
Falding and Cathcart, 59
Faurolt, C., 271
Fels, 85
Ferraris, 186
Fischer and Delmarcel, 391
Fletcher, 136
Forrer, M., 333
Foster, 120
Fowler and Medley, 168
Freeth, F. A., 398
Fremy, 394
Friedländer, A., 390
Fromont, 54
Fryer, 139
Fulda, W., 87, 158

GAILLARD, 48, 114
Garroway, 233, 391
Gay-Lussac, 145, 207
General Chemical Co., 120
Gerstenhöfer, 256
Gidden, 344
Gilchrist, 379
Gintl, 363
Glod, 368
Glover, 209
Gmelin, 315
Goldmann, 393
Gossage, 53, 339
Gothard, 345
Graeger, 343
Gräflich von Landsberg, 341
Green and Huncoat Plastic Brick and Terra Cotta Works, 248
Griesheim, 155, 169
Grosse-Leege, 62
Guthrie & Co., 188
Guttmann, C., 23, 55, 120, 220, 238

HACKER AND GILCHRIST, 75
Haesler, P. C., 402
Hähner, 401
Hallock, 389
Hallwell, 152
Hamburger, 287, 314
Hardwick, 340
Harkortsche Bergwerke und Chemische Fabriken, 117
Harris and Thomas, 29, 64, 238
Harrison Blair, 171
Hart, 188
Hart, J. A., 56
Hart and Bailey, 76
Hartmann, 27, 51, 55, 59, 83, 89
Hasenclever, 9, 51, 82, 196, 232, 256, 290
Haughton, 190
Haughton Metallic Packing Co., Ltd., 114
Hayes, 368
Heastie, B., 176
Hegeler and Heinz, 43, 233
Heinz, N. L., 86, 239, 259
Heinz and Chase, 80
Hemptine, D., 53
Hersey and Blake, 234
Herreshoff, 233
Higgins, 180
Hilbert, 395
Hoffmann, E., 60
Höfling, 43, 158, 236
Hofmann, A. W., 339, 389
Hofmann, P. W., 71
Hofmann, R., 60
Hommel, 162
Hunt, 79
Hurter, 110, 139, 198, 287, 300, 320

IMISON, 344
Inglis, 287, 288
Ising, 22, 29

JACKSON, 287
Jacobs, C. B., 390
Johnson, 391
Jones, A. O., 280
Jurisch, 202

KALINOWSKY, 31
Kaltenbach Pipe Co., 95
Kamiryo, Junichi, 384
Kauffmann, E. W., 46, 84
Kee, junr., and Wedge, 391
Kenyon and Swindells, 400
Keppler, 59
Kerl-Strohmann, 382
Kestner, P., 128, 176, 180, 185, 237
Kirkham, Hulett & Chandler, Ltd., 234
Klencke, 243
Klute and Ising, 162
Knapp, 381
Knorre and Arndt, 308
Kolb, 198, 310
Körting, 115, 122
Krantz, 31
Kretz, 139
Kubierschki, 236
Kuenzi, 394
Kuhlmann, 205, 210
Kühne, 389

LAGACHE, 283
Lamoreux, 97
Larison, E. L., 91
Lasne, 199
Laufer, 205
Laurent, 174
Leach, 344
Le Roy, 366
Lessing, R., 241
Leyland and Deacon, 2
Linder, 303
Lippmann, 10
Littman, 29, 88, 364, 366
Ludwig, 235
Lunge, 62, 71, 120, 127, 135, 152, 158, 163, 200, 204, 210, 227, 230, 256, 261, 286, 287, 289, 294, 305, 307, 309, 312, 314, 322, 325, 381, 386
Lunge and Abenius, 363
Lunge and Berl, 332
Lunge and Naef, 42, 198, 292, 294, 314, 318, 320
Lunge and Rohrmann, 244
Lutjens, J., 274
Lüttgen, 246
Lüty, 132, 154, 220, 229, 243
Lyte, M., 342

MACADAM AND WALKER, 278
McCay, L. W., 351
MacCulloch, 253
MacDowell, C. H., 49
MacDougal and Rawson, 79
Mackenzie, J., 87
Mackenzie and Laughlan, 352
Macnab, 93
Mactear, 53, 287, 291, 295, 297, 320
Manufacture de Javel, 277
Martin, 394
Mason, W., 168
Maudsley, 281, 294
Ménard-Dez, 231
Merscher, 235
Meyer, Th., 51, 55, 60, 83, 135, 295, 326, 394
Metallbank und Metallurgische Gesellschaft, 29
Middleton, S., 237
Miles, F. D., 325
Mills-Packard, 63
Mitarnowski and Benker, 204
Moity, A., 212
Monarch Manufacturing Works, 116
Moore, T. S., 356
Morancé, 342
Moritz, R., 23, 49, 96, 158, 190
Moscicki, 249, 396
Moser, 307
Mugdan, 401
Müller, A., 370

NAEF, 284, 294, 312
Nagel, 119
Nagelschmidt, 190
Nemes, 23, 49, 50, 51
Neumann, B., 401
Neumann, E. A., 32
Neumann, M., 134
Nicklès, 367
Niedenführ, 33, 72, 128, 132, 134, 155, 221, 228, 239, 245, 377
Nielsen, H., 235, 237
Nitrogen Products and Carbide Co., Ltd., 235
Noll, 168
Nörrenberg, 367
Norske Akt. f. Elektrokemisk Ind. and Halvorsen, 233
Norton, 119
Nydegger, O., 338

O'BRIEN, A. P., 128
Oliphant, J., 191
Oliver-Sherwood, 190
Opl, C., 81, 97

Oswald, 325
Otto and Löwe, 343

PANNEL, 180
Parent, 120, 234
Parrish, P., 49, 92, 337, 339
Pattinson, 363
Pauling, 168
Payen, 361, 382
Péclet, 136
Peligot, 310
Pelouze, 362
Pelouze and Frémy, 310
Pérégrin, 307
Petersen, 31, 46, 50, 59, 86, 202, 248
Plath, 184
Poley, 117
Pollak, 308
Porter, 43, 295
Prager, 120
Pratt, N. P., 55, 99, 283
Primavesi, A., 118
Prud'homme, 397

QUINAN, K. B., 93

RABE, H., 55, 76, 113, 120, 132, 135, 141, 168, 246
Ramsay, 287
Ramsbottom, 139
Raschen, 344
Raschig, 235, 288, 313, 316, 328
Reed, C. J., 96
Reese, 370
Regnault, 111
Regnault and Sorel, 142
Reynolds, O., 180
Reynoso, 389
Reusch, 157
Rheinisch-Westfälische Sprengstoff Co., 157
Riesenfeld, 391
Riley and Barnes, 355
Ritcher, 45
Roessler, 388
Rogé, 397
Rosenstand-Woldike, 363

SACHE, 114
Salessky, 234
Salom, 391
Santa, 114
Sauerbrey and Wünsche, 245
Scherb, 184
Scherfenberg, 247
Scherfenberg and Prager, 112, 120
Scheurer-Kestner, 38, 139, 226, 256 381, 394
Schliebs, 89, 134
Schmidt, F., 359
Schmiedel and Klencke, 96
Schobner and Ludwig, 238
Schoop, 236
Schott, C., 394
Schubert, 156
Schultz, F., 336, 366
Schüphaus, 114
Schütz & Co., 371
Schütze, P., 184
Schwarz, 343
Schwarzenberg, 256
Sébillot, 388
Seeck, 23
Seger, 139
Shepherd, S. W., 76, 83, 240
Sherwood, L. T., 399
Shores, 344
Simon, C., 176, 184
Simon-Carves, Ltd., 23
Skey, 362
Skinner, L. B., 404
Smith, A. K., 406
Smith, H. A., 290
Soc. anon. des Établ. Eyken et Leroy, 24
Soc. Dior fils, 397
Sorel, 67, 111, 203, 228, 261, 289 320, 322, 325
South Metropolitan Gas Co., 92
Sprengel, 105, 119
Stahl, 337
Stanton, 180
Statham & Sons, 237
Steuber & Co., 86, 217
Stinville, 266
Strype, W. G., 127, 300
Swiss Soc. le Nit., 278
Szigeti, W., 115

TARAUD AND TRUCHOT, 204
Thauny, 145
Thede, J., 48
Thermal Syndicate Ltd., 372
Thiele, 44
Thomas, D. H., 119
Thomson, 347
Thomson-Houston Co., 56, 128
Thorn, W., 247
Thyss, 66
Tjaden-Möddermann, 369
Tobler, 401
Tod, 343
Tone, F. T., 236

Trautz, 328
Treyi, 395
Tungay, S. J., 87, 251

UEBEL, 397
Unione Italiana fra Consumatori e Fabricani di Concimi e Prodotti Chemici and Antonin Sonneck, 49
United Alkali Co., Ltd., 344, 359
United States Chemical Co., 277
Universal Valve and Chemical Co., Ltd., 163
Utsunomiya, Hideo, 384

VEREIN CHEMISCHER FABRIKEN, Mannheim, 345
Verein für Chemische und Metallurgische Produktion, Aussig, Czecho-Slovakia, 369
Vogel, L., 105
Vogt, 140
Volberg, 87
Vorster, 210, 224, 226

WACKENRODER, 362
Wacker, 389
Waggaman, W. H., 90
Wagner, 400
Walter and Boeing, 53
Ward, 52
Wareing, 344
Warming, K., 276
Watson, E. R., 400
Watson, H. J., 303
Weber, R., 222, 310, 316, 392
Wedekind & Co., 394
Wedge, U., 88, 200
Welch, 64, 392
Wentzki, 56, 85
Windus, 233
Winkler, Cl., 198, 222, 312, 315
Wilczewski, F., 401
Wilde, 402
Winslow and Hart, 76
Winteler, 364
Wright, 382
Wyld and Shepherd, 76, 83, 240
Wyporek, A., 338

ZAHN, 397
Zeisberg, F. C., 249

INDEX OF SUBJECTS

ACID, cisterns, 192
dishes, drips, 101
distribution on the Gay-Lussac tower, 159
-eggs, 171
in chamber exits, testing, 296
-proof bricks, 212
pumps, 185
valves, 163
Air lifts, 191
shafts in chambers, 55
supply to chambers, 254
Anemometers, 136
Application of sulphuric acid, 403
Arrangement of acid works on the chamber plan, 373
Arsenic, de-arsenication of strong sulphuric acid, 356
injurious action of, 338
in sulphuric acid, 337
methods of removing, 340
partial removal in manufacturing process, 340
quantity present in pyrites, 337
removal as a soap, 345; as trichloride, 343; as sulphide, 346; generation of the hydrogen sulphide, 348; precipitation of the sulphide, 350; filtering and washing arsenious sulphide, 352; composition of the precipitate, 355; by crystallisation of the acid, 342; by distillation, 341
Asbestos cement and packings, 412

BISULPHATES, manufacture of sulphuric acid from, 397
Blue Welsh bricks, 212
Bricks for lining the Glover, 212
Brimstone acid, so called, 372
Burning the lead joints, 10
danger, caused by arsenical materials, 12
use of compressed gases, 12
Burns by acid, treatment of, 406

CARBON dioxide in chamber-gases, 295
Carboy syphon, 99
Cements and packings for sulphuric acid, 412
Ceratherm pumps, 188
Chamber acid-drips, 101
anemometers, 136
dampers, 125
drawing off the acid, 98
fittings, 97
glass windows (sights), 103
pressure gauges, 103
taking samples, 102
thermometers, 102
Chamber-process—
automatically regulating the supply of nitre, 276
avoiding water or weak acid, 253
causes of loss of nitre, 286
depth of acid, 283
distribution of the gases and rate of formation in various parts of the chamber, 290
formation of nitrogen peroxide, 287
irregular working, 284
starting the chambers, 252
supply of air, 254
supply of nitre, 266
supply of steam (water), 259
temperature, 278
theories of the chamber-process—
Briner & Rossignol, 334
Brode, 326
Clément and Désormes, 309
Divers, 328
Forrer, 333
Lunge, 312, 314
Ostwald, 325
Peligot, 310
Raschig, 313, 329

Chamber-process (*contd.*)—
theories of the chamber-process (*contd.*)—
Trautz, 328
Weber, 310
Winkler, 312
Chamber-space, proposal for diminishing, 52
Chimney for acid-chambers, 122
Coke, as packing for Gay-Lussac towers, 151
reducing action of, 152, 199
Colour of the chamber-gases, 269
Coloured sulphuric acid, 367
Connections for acid chambers, 41
Coolers for the acid, 194
Cooling the chambers, proposals for, 52, 63
Cost of manufacturing sulphuric acid from pyrites, 386
of repairs to chambers, 49

DE-ARSENICATION of chamber-acid, 340
De-arsenication of strong sulphuric acid, 356
Denitration of nitrous acid, 206
by steam or hot water, 207
by steam columns, 209
by the Glover tower, 209
by other means, 233
Density of sulphuric acid, tables showing, 410
Distributing apparatus for feeding the towers, 159
Draught production in lead-chambers, 120
by fans, 127
regulation of, 124
regulators, automatic, 126
Drips for acid chambers, 100
Duron system, 87

ERECTION of chambers, 2
Exit gases, testing the chamber, 296
average escapes in Great Britain, 298

FANS for production of draught, 127
part played in process by, 132
position to place, 128
Filters for arsenious sulphide, 352
Frame for acid-chambers, 7
protection against insects, 8

GASES, accidents by poisonous, 157
calculation of the volume according to temperature and moisture, 142
Gay-Lussac tower, centralised system of working, 169
cooling apparatus for the acid feed, 194
description of, 146
dimensions of, 147
distribution of the feed of acid, 159
employing plate towers, 154
exit gases from, 202
faulty working of, 201
foundations for, 148
framework of, 148
invention, 145
joining lead sheets, 149
other packings, 153
packing with coke, 151
proposals for treating exit-gases, 204
pumping the acid, 171
air-lifts, 191
Kestner elevator, 176
pulsometers, 174
pumps, 185
quantity of acid required, 196
repacking, 156
prevention of accidents in, 157
thickness of lead, 148
various other plans for recovering the nitre, 205
working the tower, 193
Glass windows (sights) in chambers, 103
Glover tower, 209
concentrating action, 226
construction, 211
cubical contents of, 219
denitration of the nitrous acid, 222
distribution of the acid, 221
formation of sulphuric acid in, 70, 227
foundations, 212
functions of, 210
height of, 217
inlet and outlet pipes for the gases, 215
lead-work, 213
material for lining, 212
position of, 221
working of, 222

HEAT of reaction in formation of acid, 119
High-pressure working of chambers, 45
Hydrofluoric acid, removal of, 369
Hydrogen for burning the lead joints, 12

IMPURITIES in sulphuric acid, 335
Insects attacking timber used in woodwork, 8
Intensive or "high-pressure" style of working, 45
Intermediate reaction towers, 66

JOISTS for chamber-tops, 18

KALTENBACH pipe process, 95

LEAD for chambers, 9
  quality of, 10
  thickness of, 9
Lead-burning, 10
Lead-chambers—
  buildings for containing acid-chambers, 32
  chamber-bottom, 19
  chamber-space used in England, 45
  combinations of chambers to form sets, 38
  connections, 41
  construction, general principles of, 1
  construction from other materials than lead, 2
  cost of repairs, 49
  cubical contents of the chambers, 44
  Falding's description of the usual English plan of building, 20
  framework, 7
  gas circulators, 51
  intensive style of working, 45
  joining the lead sheets, 10
  lead for chambers, 9
  other proposals for diminishing the chamber-space, 52
  pillars, 3
  renewal of, 35
  shape of, 38
  size of, 39
  special ways of building chambers, 22
  Benker and Millberg's system, 47
  Falding's chamber, 58
  Meyer's tangential chambers, 60
  Mills-Packard type, 63
  Moritz type, 49
  Petersen's regulator, 46
  Simon-Carves chambers, 23
Leakage of acid, 384
Lining for Glover towers, 212
Loss of nitre, causes of the, 286
Losses in manufacture of sulphuric acids, causes of, 383
Lunge plate-towers, 67

MERCURY in chambers, action of, 9
Mills-Packard chambers, 63
Mixing the gases, 52, 56, 59, 60

NITRE—
  chemical tests for nitrosity, 270
  consumption of, in manufacture, 381
  necessity for recovery of, 268
  observation of the colour of the gases, 269
  proposals for modifying the ordinary way of supply, 277
  rules for supply, 267
  supply to chambers, 266
Nitrogen compounds, recovery of, 144
Nitrogen peroxide, behaviour against sulphuric acid, 144
  question of its presence in the Gay-Lussac acids, 199
Nitrous acid, denitration of, 206

OBSIDIANITE, 248
Opl apparatus, 81

PACKED-CELL process, 91
Packings and cements, 412
Packings for Gay-Lussac and other towers, 234
  conditions essential, 234
  flints, 243
  Guttmann cells, 239
  propeller packings, 237
  rings, 242
Petersen regulator, 202
Pillars for the lead-chambers, 4
Plate towers for the manufacture of sulphuric acid, 67
Plumber's machine, 10
Poisonous gases in repacking Gay-Lussac towers, 156
Pressure gauges, 103
Processes dispensing with nitre, 388
Pulsometers, 174
Pumping apparatus, 171
Pumps, 185
Purification of sulphuric acid—
  by distillation, 370
  by electrolysis, 367
  arsenic contents, 337
  impurities in sulphuric acid, 335
  removal of arsenic, 340
  of nitrogen compounds, 361
  of selenium, 363

RECOVERY of nitrogen compounds, 144, 205
Replacing the lead-chambers entirely by towers, 79
Duron system, 87
Kalenbach pipe process, 95
Opl apparatus, 81•
Packed-cell process, 91

SAMPLING the acid in lead-chambers, 102
Selenium, removal from the acid, 363
Sights in chambers, 103
Siphons for drawing off the acid from the chambers, 99
Specific gravity, tables of, 410
Sprays, water, 109
Steam, for the chambers, 104
columns for denitration, 209
pipes for chambers, 105
quantity required, 108
regulators, automatic, 106
use of exhaust steam, 105
used for denitrating the nitrous acid, 207
Sulphur dioxide to Gay-Lussac inlet, 200
Sulphuric acid, applications of, 403
causes of loss in manufacturing, 383
costs of manufacture, 384
costs of manufacture from pyrites, 386
deviations in gravities according to temperature, 410
effect of arsenic in, 338
produced from various materials in U.S.A., 403
purification from arsenic, 340
from nitrogen compounds, 361
from selenium, 363
yields, 379
Sulphuric acid manufacture—
by electricity, 392
Sulphuric acid manufacture (*contd.*)—
by producing hydrochloric and sulphuric acids simultaneously, 401
combination of the contact-process and the chamber-process, 402
from bisulphates, 397
from sulphates, 393
processes dispensing with nitre, 388
Sulphuric acid works, general arrangements of, 373
costs of the chamber plant, 377
plans with chambers and towers, 377

TANGENTIAL chambers, 60
Tanks and cisterns, 192
Temperature of the lead-chamber process, 278
Theories of the chamber-process. *See under* Chamber-process.
Thermometers, 102
Towers, arrangement and plans for a combination of chambers and towers, 377
intermediate, for replacing chambers, 79

VALVES for acid, 163
Velocity of gas currents, measurements of the, 136
Vitreosil, 372
Volume of chamber-gases, variation with temperature, etc., 142
Volvic lava for Glover towers, 212

WATER, sprays for regulation of, 259
Water, sprays for supplying, to chambers, 109
Works, arrangement of, on the chamber-system, 373
lay-out of acid and copper extraction, 379

YIELD of sulphuric acid, 379

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